JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS
ON
ORGANIC CHEMISTRY.

495-10

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1893. Vol. LXIV. Part I.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1893.

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,
ST. MARTIN'S LANE.

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INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

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1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_3{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+2}$ as *α*-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as *β*-compounds, thus: $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = *α*-dimethylethylene; $CH_2{:}C(CH_3)_2$ = *β*-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{:}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{:}C{\cdot}C_nH_{2n+1}$. Adopt the same *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol: furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_3O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2{\cdot}COOH$, and not $C_6H_3(OC_2H_5)_2{\cdot}COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2{\cdot}NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3{\cdot}CH(OEt)_2$ instead of $CCl_3{-}CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$

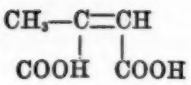
$[CCl_3{\cdot}CH(OH)]_2S$ instead of $\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}{>}S$

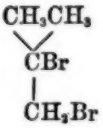
$CH_2 : CH_2$ instead of $CH_2{=}CH_2$

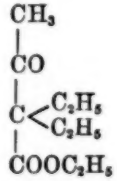
$CH : CH$ instead of $CH{\equiv}CH$

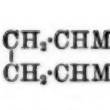
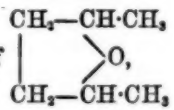
$CH : C{\cdot}CH_2{\cdot}CH_2{\cdot}C : CH$ instead of $\begin{matrix}CH_2{-}C{\equiv}CH\\|\\CH_2{-}C{\equiv}CH\end{matrix}$

$CHMe : CHPr^{\alpha}$ instead of $CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$

COOH·CH : CMe·COOH instead of 

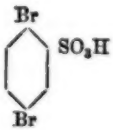
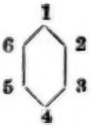
CH$_2$Br·CBrMe instead of 

CEt$_2$Ac·COOEt instead of 

 instead of 

CHPh(OBz)·CH(OBz)·COOEt instead of
C$_6$H$_5$·CH(O·CO·C$_6$H$_5$)·CH(O·COC$_6$H$_5$)·COOC$_2$H$_5$.

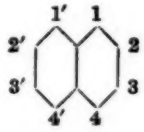
19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

Paradibromobenzenesulphonic acid, C$_6$H$_3$Br$_2$·SO$_3$H[Br : SO$_3$H : Br = 1 : 2 : 4] instead of  the figures always being used in the order 

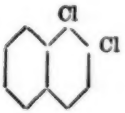
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

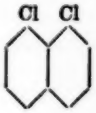
20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

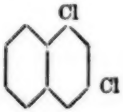
In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—

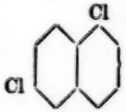


The dichloronaphthalenes, for example, are spoken of simply as 1:2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—

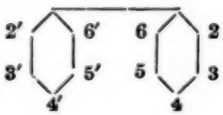
1 : 2 dichloronaphthalene = 

1 : 1′ dichloronaphthalene = 

1 : 3 dichloronaphthalene = 

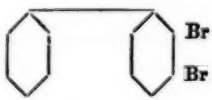
1 : 3′ dichloronaphthalene = 

In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′. as shown by the following symbol:

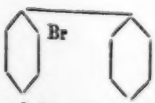


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
„ [Br = 3]
„ [Br = 4]

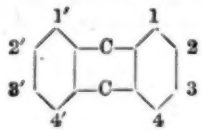
and the two dibromodiphenyls 

and



are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6′].

In the case of anthracene, employ the following symbol, and indicate the position of the radicles relatively to the central C_2-group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3'].
Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

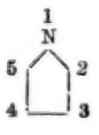
In speaking of compounds such as these, their constitution may be represented by the names

1 : 2 Dihydroxyanthraquinone		= Alizarin.
1 : 4	„	= Quinizarin.
2 : 3′	„	= Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone		= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:

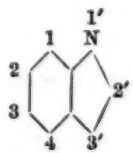
In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:



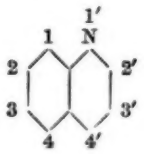
Pyrroline.

Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Mechanical Comparison between the Cyanogen Radicle and the Halogens. By G. Hinrichs (*Compt. rend.*, **115**, 177—179).—The author finds that the boiling points of cyanogen derivatives of the paraffins may be calculated correctly by means of the formulæ which he has given in former papers, if cyanogen is regarded as having the constitution usually assigned to it. In dealing with the haloïd derivatives, the halogens must be treated as simple atoms, and not as compound radicles, and the author, therefore, concludes that the chemical elements, if in reality complex in nature, cannot be compounds of the same order as the ordinary compound radicles.

H. C.

Action of Hydriodic Acid on Carbon Tetrachloride. By B. Walfisz (*Bull. Soc. Chim.* [3], **7**, 256—257).—When carbon tetrachloride (1 mol.) is heated with concentrated aqueous hydriodic acid (1 mol.) in a sealed tube for 10 hours at 130°, it is converted into iodoform and hydrogen chloride, iodine being set free. The iodine may be taken up with potash solution, or the iodoform may be distilled from the crude product.

Jn. W.

Action of Zinc on Bromo-derivatives of Tricarbon Nuclei. By Lespieau (*Bull. Soc. Chim.* [3], **7**, 260—261).—*Symmetrical tribromopropylene*, $CHBr{:}CBr{\cdot}CH_2Br$, is made by treating tetrabromallene (m. p. 9—10°) with dry potash (2 mols.) under reduced pressure. It

boils at 109—112° under a pressure of 20 mm., and attacks the eyes and skin. When poured drop by drop (15 grams) into a mixture of zinc powder (10 grams) and alcohol (10 grams of 80 per cent.) heated at 60—70°, it is converted into allylene. Tribromhydrin and allyl bromide are converted into propylene under similar conditions, and β-epibromhydrin is converted into a mixture of propylene and allylene. JN. W.

Action of Iodine on Derivatives of Acetylene. By A. PERATONER (*Gazzetta*, **22**, ii, 86—94).—The author is of opinion that hydrocarbons containing the group ·C:CH combine readily with iodine at low temperatures, and that hydrocarbons in which the acetylenic hydrogen is displaced by organic radicles do not easily take up iodine, just as they do not form metallic derivatives (compare Liebermann and Sachse, Abstr., 1892, 470). The author has prepared the compounds described below, in order to support this view.

A satisfactory yield of crotonylene is obtained on heating a solution of β-butylene dibromide (50 grams) and potash (100 grams), in absolute alcohol (150 c.c.), in an autoclave at 120° for two hours under 7 atmospheres pressure. The product is fractionated, and the vapours condensed in a freezing mixture. *Crotonylene diiodide*, CMeI:CMeI, is prepared by leaving a mixture of crotonylene (10 grams), alcohol (10 c.c.), and iodine (50 grams) in a sealed tube for 10 to 12 days. The product, after washing with dilute sulphurous acid and drying, ultimately solidifies with development of heat; it separates from alcohol or dilute acetic acid in colourless, tabular crystals, and melts at 41·5°. Under ordinary pressure, it boils at 180—190° with the liberation of much iodine; under a pressure of 22 mm., it boils at 108—110°, giving a slightly coloured distillate. It has an irritating odour recalling that of raspberries, and gives a normal molecular weight by the cryoscopic method in acetic acid solution.

Diphenyldiacetylene tetriodide, CPhI:CI·CI:CPhI, is prepared by allowing a solution of diphenyldiacetylene (2 grams), and iodine (5 grams) in carbon bisulphide (20 c.c.) to remain for eight days. The solvent is then distilled off, and the residue decolorised by sulphurous anhydride and extracted with alcohol, which leaves the iodide (0·8—1·1 gram) undissolved. It crystallises in beautiful, yellowish needles, melts at 144°, and decomposes at 150—155°. It is very sparingly soluble in the ordinary solvents, and is altered by light.

Phenylethylacetylene diiodide, CPhI:CEtI, may be obtained either by allowing a solution of phenylethylacetylene (3 grams) and iodine (6 grams) in alcohol (20 c.c.) to remain for two months, or by heating the mixture in a sealed tube at 100° for eight hours. It boils at 140—144° with slight decomposition and always contains free iodine; it has a sharp, aromatic odour, and does not solidify in a mixture of ice and salt.

Propylacetylene diiodide, CPrI:CHI, is formed with development of heat on adding iodine (40 grams) to a mixture of propylacetylene (10 grams) with alcohol (3 vols.), surrounded by a freezing mixture.

After two hours, the iodide separates as a heavy oil, which, when washed, decolorised, and dried, boils with slight decomposition at 130—133° under a pressure of 22 mm. It has an irritating odour, and is changed by light. W. J. P.

Some Derivatives of Glycerol. By A. Bigot (*Ann. Chim. Phys.* [6], **22**, 433—495).—Although this paper is very long, it contains little that is new; many of the experiments, which are described at considerable length, gave negative or indefinite results.

Hexylene dioxide, $\begin{matrix}O\\|\\CH_2\end{matrix}\!>\!CH\cdot CH_2\cdot CH_2\cdot CH\!<\!\begin{matrix}O\\|\\CH_2\end{matrix}$, is formed, together with compounds of higher boiling point, when epichlorhydrin is treated with sodium in ethereal solution; it is isolated by repeated fractional distillation (compare Hübner and Miller, *Annalen*, **154**, 186; Claus, *Ber.*, 1877, 556; and Hanriot, *Ann. Chim. Phys.* [5], **17**, 96). It is a colourless liquid, boils at 153°, and is soluble in 20 parts of boiling water, but insoluble in cold water; it combines with sodium hydrogen sulphite and with magnesium chloride, and reduces ammoniacal silver nitrate and Fehling's solution. It combines with chlorine and with bromine, yielding with the latter a solid, colourless substance, which is insoluble in all ordinary solvents. On reduction with sodium amalgam in dilute alcoholic solution, or with sodium and absolute alcohol, it yields a mixture of products from which a pure compound cannot be isolated by fractional distillation. It does not combine with cold water, but when heated with dilute sulphuric acid at 100°, it is converted into *hexylene glycol oxide*, $C_6H_{12}O_3$; this compound is a colourless, moderately mobile liquid, boils at 145° under a pressure of 20 mm., and is soluble in water, alcohol, and ether; it does not combine with water even in presence of sulphuric acid. The *diacetate*, $C_6H_{10}O(OAc)_2$, is formed when the dioxide is heated at 180° for 15 hours with excess of acetic anhydride or glacial acetic acid; it is a colourless liquid, boils at 141° under a pressure of 15 mm., and is insoluble in water, but soluble in alcohol, ether, chloroform, &c.; it is not acted on by acetic anhydride at 180°. The *chlorhydrin*, $C_6H_{10}OCl\cdot OH$, can be obtained by passing hydrogen chloride into well cooled hexylene dioxide; it is a colourless liquid, specifically lighter than water, in which it is only sparingly soluble, and when treated with potash, it is reconverted into the dioxide. The *bromhydrin*, $C_6H_{10}OBr\cdot OH$, and the *iodhydrin*, $C_6H_{10}OI\cdot OH$, prepared in like manner, resemble the chlorhydrin in properties.

When the mixture of chloriodhydrins (1 kilo.), obtained by treating allyl alcohol with iodine chloride in well cooled aqueous solution, is dissolved in ether and finely divided dry sodium hydroxide added to the warm solution in small portions at a time, a considerable development of heat occurs, and the ethereal solution becomes colourless; the various products of the reaction are separated by fractional distillation under reduced pressure, and seem to be: Allyl alcohol (about 50 grams), α-epichlorhydrin (about 50 grams), β-epichlorhydrin (about 40 grams), α-epi-iodhydrin (about 15 grams), and β-epi-iodhydrin (about 10 grams).

β-Epichlorhydrin, $O<\begin{matrix}CH_2\\CH_2\end{matrix}>CHCl$, is best isolated from the fraction boiling at 116—132°, which contains also α-epichlorhydrin, by heating the mixture at 100° for half an hour with dilute acid; the unchanged β-compound is extracted from the neutralised solution by shaking with ether, and purified by fractional distillation. It boils at 132—134°, is specifically heavier than water, and is not acted on by potassium cyanide in aqueous solution even at 100°. When treated with potassium acetate or silver acetate, it is slowly converted into compounds of high boiling point; with phosphorus pentachloride, it gives dichloropropylene, $CH_2Cl\cdot CCl{:}CH_2$, and on reduction with sodium amalgam in aqueous solution, it is converted into allyl alcohol.

When symmetrical dichlorhydrin is treated with sodium in ethereal solution, sodium chloride is deposited, propylene and hydrogen are evolved, and there remains in solution a mixture of allyl alcohol, α-epichlorhydrin, and unchanged dichlorhydrin; α-monochlorhydrin, under the same conditions, gives hydrogen, glycide, and other products.

Glycide boils at 160—161° with decomposition, and combines with water even at the ordinary temperature; when treated with hydrogen chloride, it is converted into chlorhydrin, and when heated with acetic anhydride at 170° for 12 hours, it is transformed into triacetin. It is readily acted on by acetic chloride in ethereal solution yielding two acetylchlorhydrins boiling at 218° and 230° respectively.

Diacetylchlorhydrin, $OAc\cdot CH_2\cdot CH(OAc)\cdot CH_2Cl$, is not acted on by sodium even at 120°; acetyldichlorhydrin, $CH_2Cl\cdot CH(OAc)\cdot CH_2Cl$, is readily acted on by sodium yielding allyl acetate; acetylchlorhydrin, $OAc\cdot CHCl\cdot CH_2\cdot OH$, is acted on by sodium in ethereal solution with liberation of hydrogen and formation of glycide acetate (b. p. 167—169°). F. S. K.

Characterisation of Sugars. By O. Loew (*Landw. Versuchs-Stat.*, **41**, 131—135).—The author criticises Tollens' theory as to true sugars being such only as yield levulinic acid when boiled with hydrochloric acid (Abstr., 1892, 249). He refutes Tollens' statement that his crude formose is methylanitan, and that of Fischer that methose is identical with α-acrose. N. H. M.

Formation of Dextrose from Starch. By C. J. Lintner (*Chem. Centr.*, 1892, i, 740; from *Zeit. Brauwesen*, **15**, 123—124).—According to Cuisinier (Abstr., 1887, 354), there exists in the seeds of many plants a special ferment, glykase, which is able to change the soluble product formed by the action of diastase on starch into glucose. This opinion has been supported by Geduld, and is now confirmed by the author. Dextrose may be obtained in not inconsiderable quantity, by the action of dried malt on starch, but glykase appears to be present in the largest proportion in maize, and dextrose may be conveniently prepared from that grain by the following process:—A wort containing dextrin and maltose of 20 per cent. Ball. such as is

formed by the action of malt extract on starch paste at 60—63°, until the iodine reaction is no longer given, is, either directly or after boiling and subsequently cooling to 70°, mixed with not too finely ground malt (? maize), so that the liquid is full of it. The action is allowed to proceed at 60°, until the specific rotatory power of the product becomes less than $[\alpha]_D = 53°$. As a rule, this complete conversion occurs in 30 hours, and at the outside takes 48 hours. The solution is then filtered, boiled with animal charcoal, again filtered, and evaporated on a water-bath until crystallisation commences.

Geduld states that the glykase in malt is present in an insoluble form; but from the investigations of the author, it appears to be present also in a soluble form. G. T. M.

Preparation of Isomaltose. By C. J. Lintner and G. Düll (*Chem. Centr.*, 1892, i, 886; from *Zeit. Brauwesen*, **15**, 145—146).—250 grams of potato starch was stirred into 500 c.c. of diastase solution containing 0·5 gram of crude diastase at 55°, and the product mixed with 2 litres of water at 75°. After complete liquefaction, another 0·5 gram of diastase was added, and the solution allowed to remain at 67—69° for three hours. At this stage, the iodine reaction was reddish-brown, and the solution showed $[\alpha]_D$ about 170°. The liquid was concentrated to a syrup on a water-bath, mixed with alcohol (80 per cent. vol.), and the solution added to hot alcohol with constant stirring, altogether 100 parts of alcohol were employed for each 10 parts of solid matter contained in the syrup. Under these conditions, dextrin and isomaltose were almost the sole products. The alcoholic solution was separated from the precipitate, the alcohol distilled off, and the residue fermented, in about 20 per cent. solution with the smallest possible quantity of dried yeast (2 grams of yeast to each 100 grams of solid carbohydrate). After 12—14 hours, the solution was tested with phenylhydrazine for maltose and dextrose; but, after 20 hours at the ordinary temperature, these could no longer be recognised. The solution was filtered, boiled with animal charcoal, again filtered, evaporated to a syrup, and again precipitated with alcohol. After distilling off the alcohol, the remaining syrup was again treated with alcohol, as above, but this time of 85 per cent. vol., the proportion used being 100 c.c. of alcohol to not more than 5 grams of solid substance. After cooling, the liquid was again poured off, evaporated, and treated with 90 per cent. vol. alcohol, 100 c.c. of alcohol being employed for each 5, or, with still better results, 3 grams of dry substance. After cooling, the alcoholic solution contained isomaltose with, at the most, only a very slight trace of dextrin, and this was removed by precipitation with absolute alcohol, of which so much was added that a slight turbidity, permanent at 40°, was obtained. The solution was then poured off from the syrup and fractionally precipitated anew.

The alcohol was then distilled off and the isomaltose obtained as a syrup. The carbohydrate could not be obtained pure in the solid form by precipitation with absolute alcohol, for the alcohol adhered to it when the temperature remained below 90°, and at temperatures above 90° decomposition occurred. Perfectly dry isomaltose is a

very hygroscopic substance. In the above process, the author obtained 20 per cent. of the dried starch employed as isomaltose.

G. T. M.

Higher Nitro-derivatives of Starch. By O. MÜHLHÄUSER (*Chem. Centr.*, 1892, i, 982—983; from *Dingl. polyt. J.*, **284**, 137—143). —According to Béchamp, two isomeric tetranitro-derivatives of starch, $C_{12}H_6O_6(ONO_2)_4$, are formed when a freshly prepared, cold solution of the carbohydrate in concentrated nitric acid is mixed with sulphuric acid. On the addition of water, the two compounds are precipitated, and they may be conveniently separated by digestion with alcohol, in which only one, namely, that having its ignition point at 178°, is soluble. The compound which is not taken up by alcohol ignites at 172°. The tetranitro-derivative which dissolves in alcohol is identical with that obtained in the process of the Nobel Dynamite Company, which consists in treating a solution of starch in nitric acid with the waste acids from the manufacture of nitroglycerin; and is also identical with the compound prepared by pouring into water a solution of starch in nitric acid which has been allowed to remain for some time. The process last named gave a very stable product.

The author has also succeeded in isolating two other nitro-derivatives of starch. A *penta-derivative*, $C_{12}H_{15}O_5(ONO_2)_5$, is obtained when 20 grams of rice starch, dried at 100°, is added in small portions at a time to a mixture of 100 grams of nitric acid (sp. gr. 1·501) and 300 grams of sulphuric acid (sp. gr. 1·8). The solution is allowed to remain for an hour, and is then poured into a large quantity of cold water. The precipitate is collected, washed, and freed from any simultaneously formed tetranitro-derivative by treatment with alcohol. The insoluble pentanitro-derivative ignites at 160°, does not colour potassium iodide paper at 60—70°, is insoluble in ether, and dissolves in acetone, ethyl acetate, and nitrobenzene. The existence of this pentanitro-derivative shows that the empirical formula for starch, $C_6H_{10}O_5$, must, at least, be doubled. When 40 grams of dried starch is added to 400 grams of nitric acid (sp. gr. 1·501), and, after remaining for 24 hours, 220 grams of the solution is slowly stirred into 600 c.c. of sulphuric acid at 66°, a gelatinous precipitate is obtained, which, in addition to the pentanitro-derivative, contains a *hexanitro-derivative*, $C_{12}H_{14}O_4(ONO_2)_6$. This ignites at 155°, is unstable in presence of potassium iodide at 60—70°, is insoluble in dilute alcohol and ether, but dissolves in ethyl alcohol, acetone, nitrobenzene, and acetic ether.

The nitro-derivatives of starch prepared with concentrated sulphuric acid are decomposed at 60—70°, with evolution of nitrous fumes, and are, therefore, unsuitable for blasting purposes. Their instability is, perhaps, to be attributed to the presence of a small quantity of starch containing sulphonic acid groups in the molecule. For the preparation of a nearly smokeless powder, the stable tetranitro-derivative, obtained without the aid of sulphuric acid, is best employed. It should be mixed with 3 parts of nitro-jute, kneaded with ethyl acetate, milled, and dried at 50—60°. G. T. M.

Molecular Masses of Dextrin and Gum Arabic as determined by their Osmotic Pressures. By C. E. LINEBARGER (*Amer. J. Sci.* [3], **43**, 426—428).—The author has calculated the molecular weight of gum arabic and dextrin from Pfeffer's observations on the osmotic pressures of their solutions. In each case, the results indicate that the simpler molecular formulæ, which are usually taken to represent these substances, should be multiplied by seven to get the true molecular formulæ. H. C.

Action of Secondary Capryl Iodide on Trimethylamine. By H. MALBOT and A. MALBOT (*Bull. Soc. Chim.* [3], **7**, 213—214).—An ethereal solution of secondary capryl iodide (1 mol.) is shaken with an aqueous solution of trimethylamine (1 mol.) for a week or more. The ethereal layer is washed with water to remove unchanged amine, and then fractionated; caprylene passes over at 125°, and about half the original amount of capryl iodide remains unchanged, dissociating, however, at a slightly higher temperature. The aqueous layer contains unchanged trimethylamine, together with the hydriodide, from which the base is recovered by treatment with silver oxide. The formation of caprylene in the cold is evidently due to the simple transference of the elements of hydrogen iodide from the capryl iodide to the trimethylamine. JN. W.

Glycolaldehyde. By W. MARCKWALD and A. ELLINGER (*Ber.*, **25**, 2984—2985).—The authors have prepared the glycolaldehyde, $OH{\cdot}CH_2{\cdot}CHO$, recently described by Fischer and Landsteiner, by a method which gives a better yield of the substance. The starting point is Pinner's glycol-acetal (this Journal, 1872, 407), which may be readily prepared in quantity; Pinner states that the hydrolysis does not proceed smoothly with mineral acids, but the authors find that if very dilute acids be employed, the hydrolysis may be readily effected. The acetal is boiled with an equal volume of water and a few drops of hydrochloric acid or sulphuric acid, a portion of the alcohol formed being allowed to distil off. The boiling is continued until oily drops no longer separate on the addition of large quantities of water, and the product is then distilled. Alcohol first passes over, mixed with very little aldehyde, and then a mixture of aldehyde and water, the residue finally commencing to decompose. A concentrated solution of glycolaldehyde may be obtained by using sulphuric acid as the hydrolysing agent, and precipitating it with barium carbonate, after distilling off the alcohol. The authors confirm the description of the properties of glycolaldehyde given by Fischer and Landsteiner, with the exception of the extent to which it volatilises in a current of steam, which they find to be considerably greater than that observed by the latter investigators. H. G. C.

Specific Gravity of Aqueous Solutions of Acetone. By K. P. MACELROY and W. H. KRUG (*Chem. Centr.*, 1892, ii, 158; from *J. Anal. Chem.* **6**, 187—188).—The acetone employed was purified by repeated distillation over calcium chloride; it boiled at 56·4°. The table gives the specific gravity at various temperatures referred to water at 4°; the weighings were not reduced to vacuum-weighings.

Acetone per cent.	15°.	20°.	25°.	Acetone per cent.	15°.	20°.	25°.
100	0·79726	0·79197	0·78630	45	0·93518	0·93091	0·92678
95	—	0·80748	0·80205	40	0·94488	0·94075	0·93691
90	—	0·82197	0·81653	35	0·95293	0·94931	0·94547
85	—	0·83588	0·83073	30	0·96092	0·95748	0·95411
80	—	0·84981	0·84454	25	0·96783	0·96490	0·96221
75	0·86442	0·86129	0·85533	20	0·97444	0·97210	0·96961
70	0·88085	0·87545	0·87073	15	0·98038	0·97831	0·97604
65	0·89271	0·88785	0·88282	10	0·98681	0·98513	0·98342
60	0·90447	0·89953	0·89477	5	0·98921	0·99169	0·98979
55	0·91526	0·91054	0·90603	0	0·99160*	0·99826	0·99712
50	0·92549	0·92051	0·91673				

The sp. gr. of pure acetone (water at 4° = 1) at various temperatures is given below:—

15°.	16°.	17°	18°.	19°.	20°.	21°.
0·79726	0·79620	0·79514	0·79408	0·79302	0·79197	0·79107

22°.	23°.	24°.	25°.
0·78988	0·78869	0·78750	0·78630

C. F. B.

Condensation of Acetaldehyde with Acetone. By L. Claisen (*Ber.*, **25**, 3164—3166).—The author failed to obtain ethylideneacetone by the action of dehydrating agents on a mixture of acetaldehyde and acetone, probably because of the formation of paraldehyde, which has almost the same boiling point as ethylideneacetone, and cannot, therefore, be separated from it. Acetaldehyde and acetone combine in the presence of dilute alkalis, alkali carbonates, or cyanides, forming *hydracetylacetone*, $OH{\cdot}CHMe{\cdot}CH_2{\cdot}COMe$, a compound intermediate between aldol and diacetonic alcohol (this Journal, 1876, i, 365), the trichloro-derivative of which has been described by Königs (Abstr., 1892, 694). It is a liquid of ketone-like odour, miscible in all proportions with water, boils at 77—78° (19 mm.), and has a specific gravity at 15° = 0·978. It boils at the ordinary pressure at 176—177° with scarcely any decomposition, and yields a *hydrazone* melting at 86—87°.

Ethylideneacetone, $CHMe{:}CH{\cdot}COMe$, is obtained when hydracetylacetone is boiled for some time with acetic anhydride. It is a colourless liquid, boiling at 122°; it has an odour resembling crotonaldehyde, but less pungent, and a specific gravity at 15° = 0·861. Experiments are in progress on the action of formaldehyde on acetone.

A. R. L.

Derivatives of Trimethylene Chlorobromide. By P. Blank (*Ber.*, **25**, 3040—3047).—*γ-Thiodibutyramide*, $S(C_3H_6{\cdot}CONH_2)_2$, is obtained by dropping γ-thiodibutyronitrile (Gabriel, Abstr., 1890, 1221) into concentrated sulphuric acid (4 parts) cooled by ice, diluting

* This figure seems to be a misprint, probably for 0·99916.

with water, precipitating the sulphuric acid by barium carbonate, and evaporating the filtrate. It crystallises in mushroom-like aggregates of delicate needles, melts at 152°, and gives γ-thiodibutyric acid (*loc. cit.*) on hydrolysis. The latter yields on oxidation *γ-sulphonedibutyric acid*, $SO_2(C_3H_6{\cdot}COOH)_2$.

Ethyl γ-cyanopropylmalonate, $CN{\cdot}C_3H_6{\cdot}CH(COOEt)_2$, is formed by boiling a solution of sodium (1·19 grams) in absolute alcohol (20 c.c.) with ethyl malonate (16·3 grams) and γ-chlorobutyronitrile (9·5 grams), in a reflux apparatus for three hours, driving over the unaltered nitrile in a current of steam, and extracting the residual oil with ether. After twice fractionating, it passes over at 290—295°.

γ-Anilidobutyronitrile, $NHPh{\cdot}C_3H_6{\cdot}CN$, is produced when γ-chlorobutyronitrile is heated on the water-bath for three hours with aniline (3 parts); the *platinochloride* melts at 191° with decomposition.

γ-Piperidylbutyronitrile, $C_5NH_{10}{\cdot}C_3H_6{\cdot}CN$, prepared by gradually adding γ-chlorobutyronitrile (48·6 grams) to piperidine (40 grams), cooled by ice, shaking the mixture, and driving over the unaltered reagents in a current of steam, boils at 241—245°. The *platinochloride* melts at 171—172°, and the *picrate* at 113—115°. When the nitrile is heated with concentrated hydrochloric acid (5 parts) in a sealed tube at 100° for three hours, *γ-piperidylbutyric acid*, which yields a *picrate* melting at 158°, is obtained; whilst if it is dissolved in absolute alcohol (27 parts) and boiled with sodium (2 parts), *δ-piperidylbutylamine*, $C_5NH_{10}{\cdot}C_4H_8{\cdot}NH_2$, which boils at 225° (743 mm.), and gives a *platinochloride* melting at 215°, is formed.

When a solution of γ-phenoxybutyronitrile (Gabriel, Abstr., 1892, 131) in 5 per cent. alcoholic ammonia (8 parts) is saturated with hydrogen sulphide, heated at 100°, and the solvent evaporated, ether extracts from the residue *γ-phenoxybutyrothiamide*, $OPh{\cdot}C_3H_6{\cdot}CS{\cdot}NH_2$, which crystallises from water in long needles; the smaller portion, insoluble in ether, separates from hot water in needles, melts at 176° with decomposition, and is *phenoxybutyramidine thiosulphate*, $[OPh{\cdot}C_3H_6{\cdot}C(NH){\cdot}NH_2]_2,H_2S_2O_3$.

When δ-phenoxybutylamine hydrobromide (6 grams) is heated with fuming hydrobromic acid (20 c.c.) in a sealed tube at 150° for 4—5 hours, and the product evaporated to dryness, the residue gives pyrrolidine on distillation with potassium hydroxide solution, and by fractional precipitation with picric acid *δ-bromobutylamine picrate*, $CH_2Br{\cdot}C_3H_6{\cdot}NH_2,C_6H_3N_3O_7$, which crystallises in leaflets and melts at 105°, is obtained.

When paracresol (50 grams) and trimethylene chlorobromide (82 grams) are added to a solution of sodium (10·6 grams) in absolute alcohol (120 c.c.), the mixture warmed on the water-bath for about three hours, and water added, an oil separates; on distilling this, the main portion consisting of *γ-chloropropyl paratolyl ether*, $CH_2Cl{\cdot}C_2H_4{\cdot}OC_6H_4Me$, passes over at 252—260° (754 mm.), whilst the fraction boiling above 300° is *trimethyleneglycol diparatolyl ether*, $C_3H_6(OC_6H_4Me)_2$, which crystallises from alcohol in slender, felted needles, and melts at 94°. If γ-chloropropyl paratolyl ether (33 grams) is boiled with a mixture of ethyl malonate (28·8 grams) and sodium (4·12 grams) dissolved in absolute alcohol (66 grams) for 11 hours, it

yields *ethyl paracresoxypropylmalonate*, which is converted into the *potassium salt* by heating it with 30 per cent. alcoholic potash; the corresponding *acid*, $MeO{\cdot}C_6H_4{\cdot}C_3H_6{\cdot}CH(COOH)_2$ melts at 116—119°. On heating the latter until the evolution of gas ceases, *δ-paracresoxyvaleric acid*, $C_7H_7O{\cdot}C_4H_8{\cdot}COOH$, passes over at 325°; it melts at 96°. By heating this with phosphorus pentachloride, and treating the resulting chloride with dilute ammonia, it furnishes the *amide*, $C_7H_7O{\cdot}C_4H_8{\cdot}CONH_2$, which crystallises from dilute alcohol in long, felted needles, and melts at 152°.

When δ-paracresoxyvaleric acid is distilled with lead thiocyanate, the corresponding *nitrile* passes over between 296° and 310°; it is converted into *ε-paracresoxyamylamine*, $MeO{\cdot}C_6H_4{\cdot}C_5H_{10}{\cdot}NH_2$, by treatment with the requisite amount of sodium dissolved in absolute alcohol; the *hydrochloride* melts at 188°, and the *platinochloride* at 202° with decomposition. When the last-mentioned base is heated in a sealed tube at 150° for five hours with fuming hydrobromic acid, it gives *ε-bromamylamine*, $CH_2Br{\cdot}C_4H_8{\cdot}NH_2$, which is isolated by means of its *picrate* (m. p. 108—110°). A. R. L.

An Index to the Literature of Angelic and Tiglic Acids from 1842 to 1892. By H. P. Talbot (*Technol. Quart.*, **5**, Nos. 1 and 2).—A summary of the various investigations on angelic and tiglic acids, accompanying an index (both of authors and subjects) to the literature of the subject. The index is believed to be practically complete to April, 1892.

Succinic Acid. By A. Rau (*Chem. Centr.*, 1892, ii, 155—157; from *Revue Hygiene*, **14**, 225—242).—The following amounts of succinic acid are dissolved at 15° by 100 parts of the solvents named:—Anhydrous ether, 1·193; alcohol, 96 per cent., 9·986; 90 per cent., 11·984; methyl alcohol, 15·73; acetone, 5·54. To estimate succinic acid in an alcoholic liquid, it is concentrated to a syrup, extracted repeatedly with boiling alcohol, the filtered extract evaporated, the residue dissolved in a little hot water, cooled, filtered, barium nitrate and 3—4 vols. of 90 per cent. alcohol added, and the whole stirred vigorously. The precipitate is collected on a filter, washed with 70 per cent. alcohol, warmed with sodium carbonate, filtered, the filtrate neutralised with nitric acid, evaporated to a small bulk, neutralised with ammonia, magnesia mixture (prepared from the nitrate) added, and the whole allowed to remain for 3—4 hours. It is then filtered, heated with potash until the ammonia is expelled, filtered, and neutralised with nitric acid. The liquid is concentrated to 100—150 c.c., precipitated with dilute silver nitrate (1 : 20), and the precipitate collected on a weighed filter, dried, and weighed. If the original liquid contained chlorides, these must be estimated on a separate sample, and a correction applied to the above result.

Wines examined contained from 0·317 (in a sample of Pfälzer wine) to 1·512 grams (in a sample of genuine sour Tokay) of succinic acid per litre. Experiments were made on the fermentation of 15 per cent. solutions of cane sugar, pure grape sugar, and maltose, at 15°, 25°,

and 35°; to each 100 c.c. of the solution were added 25 c.c. of a solution of 25 grams of acid potassium phosphate, 8·5 grams of silver sulphate, and 20 grams of asparagine per litre, to serve as food for the ferment. It appears that the formation of succinic acid is not diminished by a lowering of temperature, nor is it increased by the addition of the food-solution; precisely the opposite is true of the formation of glycerol. The presence or absence of air has no effect on the formation either of glycerol or of succinic acid. The more energetic the action of the yeast cells, the more succinic acid is usually formed. It seems thus that succinic acid is a normal product of the alcoholic fermentation, and its formation does not depend on a simultaneous production of glycerol. C. F. B.

Decomposition of the Ethyl Salts of some Chloro-β-ketonic Acids by Dilute Sulphuric Acid. By A. PERATONER (*Gazzetta*, 22, ii, 37—44).—Ethyl chloroxalacetate (30 grams), when boiled for an hour with dilute (1 : 5) sulphuric acid (150 c.c.) in a reflux apparatus, gives off very little carbonic anhydride. The product yields a resinous substance with phenylhydrazine, but on treating it with barium hydroxide, and subsequently removing the excess of barium, barium oxalate is obtained. The filtrate from this, after concentration, yields crystals of barium chloracetate, and on again filtering and treating with silver nitrate, a precipitate of silver chloracetate is thrown down. The hydrolysis, therefore, proceeds in accordance with the equation

$$COOEt\cdot CO\cdot CHCl\cdot COOEt + 3H_2O = H_2C_2O_4 + CH_2Cl\cdot COOH + 2EtOH.$$

Ethyl chloracetoacetate, when similarly treated, evolves much carbonic anhydride, and monochloracetone is obtained on distilling the product. On prolonged heating, the ethyl salt decomposes, with formation of monochloracetic acid.

Ethyl chlorobenzoylacetate, when treated with dilute sulphuric acid, yields ω-chloracetophenone, which may be separated by distillation in a current of steam; the aqueous distillate also contains benzoic acid, and monochloracetic acid is produced during the hydrolysis.

W. J. P.

Specific Gravities of some Isomeric Acids. By S. TANATAR and C. TCHELEBIEFF (*J. Russ. Chem. Soc.*, **22**, 548—549).—The authors have made determinations of the specific gravities of various pairs of solid isomeric acids, using a pyknometer with australene (in which the substances are insoluble) as liquid. Their results are exhibited in

Acid.	Sp. gr.	Mol. vol.
Fumaric	1·625	71·38
Maleïc	1·590	72·95
Succinic	1·554	75·93
Isosuccinic	1·455	81·09
Dimethylsuccinic (fumaroïd)	1·314	111·11
,, (maleïnoïd)	1·339	109·03

the accompanying table, the temperature of experiment being 18·5° to 20°, and water of the same temperature being chosen as standard.

J. W.

Oxidation of Diallyloxalic Acid by Potassium Permanganate. By S. Phokin (*J. Russ. Chem. Soc.*, **22**, 522—535).—A neutral solution of the potassium salt of diallyloxalic acid was cooled in ice, and to it there was added drop by drop a 1 per cent. solution of potassium permanganate, in such quantity that to 1 mol. of acid there were 2—3 atoms of available oxygen. On the following day, the solution was filtered from the oxide, and treated with carbonic anhydride. A portion was investigated for neutral organic substances, but none were found. The bulk of the solution was then treated with sulphuric acid, corresponding with the amount of potassium present, and distilled. The acid distillate was found to contain nothing but formic acid. In order to obtain the non-volatile substances in the solution which remained, it was extracted first of all with ether. In the ethereal extract unchanged diallyloxalic acid, oxalic acid, and some formic acid were found. The aqueous portion was now evaporated to dryness, and treated with alcohol, in which all the organic substances dissolved. In order to remove the oxalic acid, the aqueous solution of the extract was treated successively with lead carbonate and hydrogen sulphide; the filtrate from the sulphide precipitate was again evaporated to dryness and extracted with alcohol. On evaporating the alcohol, a syrupy mass was left; this was the chief product of the oxidation, and consisted of a mixture of tetrahydroxyoctolactone and a lactonic acid.

The *lactonic acid*, $C_7H_{10}O_6$, is probably

$$COOH\cdot CH_2\cdot C(OH)<\begin{matrix}CH_2\\COO\end{matrix}>CH\cdot CH_2\cdot OH.$$

The calcium salt of the bibasic acid, corresponding with this lactonic acid, is very slightly soluble in water, and advantage was taken of this property in order to separate the two products of oxidation, these being boiled up with calcium hydroxide and water. In order to obtain the free lactonic acid, the calcium salt was dissolved in acetic acid, and decomposed by precipitation with oxalic acid; the solution was filtered, and the filtrate boiled to get rid of acetic acid. The oxalic acid present was then removed, and the pure lactonic acid, which forms a thick, yellow syrup, was obtained as above. Its barium salt, $Ba(C_7H_9O_6)_2$, may be obtained by treating it with barium carbonate, filtering, and precipitating with alcohol. The barium salt of the bibasic acid, $BaC_7H_{10}O_7$, is a gummy mass, whilst the calcium salt, $CaC_7H_{10}O_7$, is pulverulent, and nearly insoluble in water.

Tetrahydroxyoctolactone, $C_8H_{14}O_8$, probably

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot C(OH)<\begin{matrix}CH_2\\COO\end{matrix}>CH\cdot CH_2\cdot OH,$$

forms a syrup having a sweet taste. The calcium salt of the corresponding acid, $Ca(C_8H_{13}O_7)_2 + 2H_2O$, is soluble in water. The barium salt is a yellow, vitreous mass, and anhydrous. The acid can form basic barium and calcium salts.

Bulitch (*J. Russ. Chem. Soc.*, **19**, 73) found a tetrahydroxyoctolactone amongst the products obtained on oxidising diallyloxalic acid by means of nitric acid. The authors consider this lactone to be isomeric, and not identical, with theirs, and think it probably has the formula $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot C(OH) < \begin{matrix} CH(OH) \\ COO \end{matrix} > CH \cdot CH_3$.

J. W.

Action of Bromine on Closed Chain Hydrocarbons in presence of Aluminium Bromide. By V. Markovnikoff (*Compt. rend.*, **115**, 440—442).—The author's researches lead to the conclusion that the action of bromine on naphthenes in presence of aluminium bromide at the ordinary temperature, affects chiefly the hydrogen atoms of the closed chain, and converts the open chain into a benzene ring, in which all the hydrogen atoms are displaced by bromine whilst the lateral chains remain intact. To this rule, however, the simplest naphthene, C_6H_{12}, is an exception, since it yields no hexabromobenzene. So far, results have been obtained up to C_9 only, and all attempts to obtain crystalline products from napthenes of C_{10} and higher have failed. It would seem that the formation of crystalline products becomes more and more difficult as the complexity of the lateral chains increases; propylnaphthene, for example, yields only a very small quantity of crystalline tribromopseudocumene.

When the hydrocarbons contain only methyl groups, the reaction gives definite results, and can be used for the qualitative detection of naphthenes. A very small fragment of aluminium is allowed to burn in a test tube containing about 0·5 gram of bromine, and after the latter has cooled, 3 or 4 drops of the hydrocarbon under examination are added. There is an immediate reaction, and after the excess of bromine has been expelled by evaporation, microscopic crystals are seen, impregnated with an oily liquid.

In some cases there is transposition of the lateral chains. Octonaphthene, for instance, always yields tetrabromoparaxylene, although in its other reactions it behaves as hexahydrometadimethylbenzene. Bromine, under the conditions indicated, acts on the derivatives of the naphthenes as well as on the naphthenes themselves.

C. H. B.

Suberene, a New Hydrocarbon. By V. Markovnikoff (*Compt. rend.*, **115**, 462—464).—Amongst the products of the action of fuming hydriodic acid on suberonyl alcohol at 280° (Abstr., 1890, 728) is a hydrocarbon, C_7H_{14}, which has hitherto been regarded as heptamethylene. This hydrocarbon, however, does not yield crystalline products with bromine in presence of aluminium bromide, if the action is allowed to continue for a short time only, but if these substances are allowed to react for several days in a sealed tube, pentabromotoluene is obtained. It would seem, therefore, that the supposed heptamethylene is really hectanaphthene or hexahydrotoluene, and it would follow that suberone is probably a derivative of heptanapthene, but this last conclusion cannot be regarded as established.

When suberonyl iodide is allowed to act on zinc for several days, with repeated addition of small quantities of hydrochloric acid, a hydrocarbon is obtained, which, after distillation over sodium, boils at

117°; sp. gr. = 0·8253. It reacts readily with bromine in presence of aluminium bromide, and after about 12 hours is converted into a crystalline mass of small needles of pentabromotoluene. The conditions under which this hydrocarbon is produced render it very improbable that any isomeric change takes place at the moment of its formation. Its high boiling point and specific gravity indicate that it belongs to a hitherto unknown series of hydrocarbons, and the author gives it provisionally the name *suberene*. C. H. B.

Hexiodobenzene. By G. E. Shaw (*Chem. News*, **66**, 141).—By heating 250 grams of iodine with 100 c.c. of pure benzene and 200 c.c. of strong sulphuric acid for a few hours daily during 10 days, a product was obtained containing, in addition to mono- and di-iodobenzene, *hexiodobenzene*; this was separated by means of its comparative insolubility in alcohol and benzene. By crystallisation from carbon bisulphide and treatment with animal charcoal it was obtained in white needles, melting at 248° (corr.); it is freely soluble in aniline and nitrobenzene. D. A. L.

Preparation of *a*-Trinitrotoluene. By C. Häussermann (*Zeit. ang. Chem.*, 1891, 661—662).—Toluene may be converted into its trinitro-derivative in a single operation; but in practice it is better to start from dinitrotoluene, which is readily obtained pure by mixing 100 parts of paranitrotoluene gradually with a mixture of 75 parts of 92 per cent. nitric acid and 150 parts of sulphuric acid. The acid mixture must be poured into the nitrotoluene, and the temperature should at first not exceed 60—65°. After all the acid has been added, the whole is heated for half an hour up to 80—85°, and the acid is then separated from the crude product. This is composed of a crystalline mass, solidifying at 69·5°, and is completely free from the mono- or tri-nitro-derivative. A formation of isomeric compounds does not take place, and even oxidation products are only present in traces; in fact, the reaction is almost quantitative.

The trinitro-derivative is obtained when the dinitro-compound is dissolved, by the aid of a gentle heat, in four times its weight of sulphuric acid, and carefully mixed with 1·5 times its weight of (92 per cent.) nitric acid, then finally heated up to 90—95°. The solution, which is at first clear, soon becomes turbid, and a layer of a clear, yellow oil accumulates on the surface and gradually increases. The reaction may be considered as finished when the slight evolution of gas completely ceases, which is generally the case after four or five hours. The operation is then stopped, and after the removal of the undecomposed acid, the residue is washed first with hot water, and finally with very weak soda solution. From 100 parts of dinitrotoluene, about 105 parts of the trinitro-product are obtained in the form of a nearly white, well crystallised mass, which in its crude state solidifies at 79°. When recrystallised from hot alcohol, its melting point is raised to 81·5°.

If, for its preparation, use is made of ordinary commercial dinitrotoluene (melting point 60—64°), the action does not proceed so quietly, and red fumes are evolved, showing a partial decomposition of the

substance. Although a pure product is finally obtained, the yield of the compound is about 10 per cent. less than in the process described, and there is also a great waste of nitric acid. It must also be remembered that trinitrotoluene is not absolutely insoluble in hot water, so that over-washing may cause serious loss. It is also slightly decomposed on prolonged treatment with alkalis or even their carbonates. L. DE K.

Dinitrochlorotoluene and the Synthesis of Azine Dyes. By R. NIETZKI and E. REHE (*Ber.*, **25**, 3005—3009).—*Dinitrochlorotoluene*, [Me : Cl : NO_2 : NO_2 = 1 : 2 : 3 : 5] is obtained by adding orthochlorotoluene (1 part) to a well-cooled mixture of nitric acid (sp. gr. = 1·48, 3 parts) and concentrated sulphuric acid (9 parts). The reaction is completed by heating at 80° for a few hours, and the mixture is then poured on to ice. It crystallises from alcohol in almost colourless needles, melts at 45°, and is easily soluble in alcohol and ether. When heated with alcoholic ammonia, it yields the dinitro-orthotoluidine melting at 208°, and when boiled with alcoholic potash, it yields the dinitro-orthocresol, melting at 85°. When reduced with stannous chloride, it is converted into a *chlorotoluylenediamine*; this crystallises from water in needles, melts at 73°, and yields well crystallised salts, and a diacetyl derivative when treated with acetic anhydride. Dinitrochlorotoluene, like the corresponding benzene derivative, reacts with amines, and the chlorine atom is replaced by the amido-group. With aniline, it yields *dinitrotolylphenylamine*, which crystallises in beautiful, red plates, and melts at 169°. With paraphenylenediamine, it yields dinitrotolylamidophenylamine and tetranitroditolylparaphenylenediamine.

Dinitrotolylamidophenylamine crystallises from alcohol in black needles, melts at 170°, and dissolves in hot dilute sulphuric acid, from which solution a yellow sulphate is precipitated on cooling. The *acetyl* derivative melts at 210°.

Tetranitroditolylparaphenylenediamine crystallises from nitrobenzene in small, brownish-red needles, and melts above 330°.

By the action of dinitrochlorotoluene on dimethylparaphenylenediamine, a base is obtained which crystallises in brownish-black needles, is easily soluble in hot dilute mineral acids, and on reduction with stannous chloride and hydrochloric acid is easily converted into the base $C_6H_2Me(\overset{6}{N}H_2)_2{\cdot}\overset{2,4}{N}H{\cdot}\overset{1}{C_6}H_4{\cdot}\overset{4}{N}Me_2$. This only differs from the leuco-base of toluylene-blue in the position of the methyl group, which in the latter is meta- relatively to the amido-group. The *hydrochloride* is very easily oxidised, and cannot therefore be obtained pure.

The *azine*, $NH_2{\cdot}C_6H_2Me{:}N_2{:}C_6H_3{\cdot}NMe_2$, is obtained by heating the stannochloride of the preceding base (30 grams), dissolved in water (1 litre), and previously neutralised with calcium carbonate, with Weldon mud (30 grams, 60 per cent. MnO_2) on the water bath. It crystallises from dilute alcohol in beautiful needles, having a coppery lustre, and does not contain water after drying at 100°. The aqueous solution is yellowish-brown; the ethereal solution exhibits a greenish-yellow fluorescence. The salts are very similar to those of toluylene-

red, but impart a yellower shade to fibres. It dissolves in concentrated sulphuric acid forming a green solution, which on dilution turns blue and then red. E. C. R.

Orthocyano- and Orthonitro-benzyl Chloride. By H. CASSIRER (*Ber.*, **25**, 3018—3030).—*Phenoxyorthotoluonitrile*, $OPh\cdot CH_2\cdot C_6H_4\cdot CN$, is prepared by adding orthocyanobenzyl chloride (7·65 grams) dissolved in alcohol (25 c.c.) to a solution of sodium (1·15 grams) and phenol (4·7 grams) in alcohol (30 c.c.), and heating the mixture on the water-bath until it has a neutral reaction, when the compound separates. It crystallises from light petroleum in white needles, and melts at 63—65°. The *thiamide*, $OPh\cdot CH_2\cdot C_6H_4\cdot CS\cdot NH_2$, is obtained when the nitrile (5 grams) is dissolved in alcoholic ammonia (10 c.c.), and the solution saturated with hydrogen sulphide and heated in a sealed tube at 100° for two hours. It crystallises from dilute alcohol in slender, bright-yellow needles, and decomposes when treated with zinc and hydrochloric acid. An attempt to reduce phenoxyorthotoluonitrile with zinc and hydrochloric acid was also unsuccessful, and no characteristic compounds were obtained by the action of concentrated sulphuric acid on this compound.

Ethoxyorthotoluonitrile, $OEt\cdot CH_2\cdot C_6H_4\cdot CN$, is prepared by heating orthocyanobenzyl chloride (7·65 grams) dissolved in alcohol (20 c.c.) with a solution of sodium (1·15 grams) in alcohol (40 c.c.) on the water-bath. After distilling off the alcohol, the compound remains as an oil; it boils at 242°, and gives γ-phthalimidine (Abstr., 1887, 1038) when dissolved in cooled concentrated sulphuric acid. The *thiamide*, $OEt\cdot CH_2\cdot C_6H_4\cdot CS\cdot NH_2$ melts at 84°.

When orthocyanobenzyl chloride is dissolved in 75 per cent. acetic acid, and the solution, after being saturated with hydrogen chloride, is heated in a sealed tube at 100°, it yields phthalimide and ammonium chloride.

Orthocyanodiphenylmethane, $CN\cdot C_6H_4\cdot CH_2Ph$, is obtained when orthocyanobenzyl chloride (10 grams) is boiled with benzene (50 c.c.) and aluminium chloride (10 grams) for 12 hours. It boils at 313—314°, melts at 19°, and is insoluble in light petroleum. When the compound is heated in a sealed tube at 170—180° with hydrochloric acid (sp. gr. 1·19), orthobenzylbenzoic acid (m. p. 117°) is produced; whilst if heated in a sealed tube at 100° with a solution of hydrogen chloride in 75 per cent. acetic acid, *orthobenzylbenzamide*, $CH_2Ph\cdot C_6H_4\cdot CO\cdot NH_2$, is formed; this crystallises from alcohol in white needles, and melts at 163°. It also yields the *nitro*-derivative, $CN\cdot C_{13}H_{10}\cdot NO_2$, on treatment with fuming nitric acid, and when it is cautiously heated on the water-bath with concentrated sulphuric acid, a mixture of anthranol and anthraquinone is obtained.

Orthobenzylbenzylamine, $CH_2Ph\cdot C_6H_4\cdot CH_2\cdot NH_2$, is produced in small quantity when a solution of orthocyanodiphenylmethane (10 grams) in alcohol (200 c.c.) is heated in a reflux apparatus with sodium (20 grams); the *hydrochloride* melts at 220°, and the *platinochloride* at 197°. The *thiamide*, $CH_2Ph\cdot C_6H_4\cdot CS\cdot NH_2$ is formed when a solution of the cyano-compound in alcoholic ammonia is

saturated with hydrogen sulphide, and heated at 100° in a sealed tube; it melts at 153°.

Orthocyanophenyltolylmethane, $CN\cdot C_6H_4\cdot CH_2\cdot C_6H_4Me$, is obtained by heating together orthocyanobenzyl chloride, toluene, and aluminium chloride. It boils at 324—326° (750 mm.) or at 296° (89 mm.), and, when heated at 100° with a saturated solution of hydrogen chloride in 75 per cent. acetic acid, yields the *amide*, $NH_2\cdot CO\cdot C_6H_4\cdot CH_2\cdot C_6H_4Me$, which crystallises from benzene in white leaflets, and melts at 123°.

Ethyl diorthocyanobenzylcyanacetate, $CN\cdot C(CH_2\cdot C_6H_4\cdot CN)_2\cdot COOEt$, is obtained when a solution of orthocyanobenzyl chloride (15·1 grams) dissolved in alcohol (20 c.c.) is added to a mixture of ethyl cyanacetate (11·3 grams) and sodium (2·3 grams) dissolved in alcohol (40 c.c.). It separates from dilute alcohol in white, rhombic crystals, melts at 122—123°, and when heated on the water-bath with normal alcoholic potash yields the corresponding *acid*; this melts at 160° with evolution of carbonic anhydride and the formation of *diorthocyanobenzylacetonitrile*, a compound which crystallises from dilute alcohol in tufts of needles, melts at 130°, and is insoluble in ether. Ethyl dibenzylcyanacetate is obtained in a similar manner from benzyl chloride and ethyl cyanacetate; on hydrolysis with alcoholic potash, it gives the *acid* $CN\cdot C(CH_2Ph)_2\cdot COOH$, which separates from alcohol in granular crystals, and melts at 188—189° with evolution of carbonic anhydride, and the formation of dibenzylacetonitrile (Abstr., 1888, 705).

Orthonitrobenzyl thiocyanate, $NO_2\cdot C_6H_4\cdot CH_2\cdot SCN$, is prepared by heating a solution of orthonitrobenzyl chloride (25 grams) in alcohol (75 c.c.) with potassium thiocyanate (15 grams) for an hour on the water-bath; it is precipitated on adding water, separates from dilute alcohol in rhombic crystals, and melts at 75°; it exerts an irritating effect on the mucous membrane. When an alcoholic solution is heated on the water-bath in a reflux apparatus with 3½ times its weight of stannous chloride and hydrochloric acid (sp. gr. 1·19) for two hours, *orthamidobenzyl thiocyanate* is formed and can be isolated in the usual manner; it crystallises from hot water in almost colourless, thick needles, and melts at 137—138°. The *hydrochloride* forms silky needles, and melts at 212°; the *platinochloride* melts at 215—217°; and the *picrate* melts at 223° with decomposition.

If orthonitrobenzyl thiocyanate is dissolved in alcoholic ammonia, and a current of hydrogen sulphide passed through the solution for two hours, a yellow compound insoluble in water and in acids is obtained; after crystallisation from alcohol, it melts at 112—113°, and is probably *orthonitrobenzyl bisulphide*, $S_2(CH_2\cdot C_6H_4\cdot NO_2)_2$. A compound having properties different from those of the substance last mentioned has been described as orthonitrobenzyl bisulphide by Jahoda (Abstr., 1890, 488), and the author suggests that the latter is perhaps the corresponding mercaptan $NO_2\cdot C_7H_6\cdot SH$. A. R. L.

Preparation of Optically Inactive Cymene from Oil of Caraway. By L. Volpyan (*Chem. Centr.*, 814—815; from *Pharm. Zeit. Russ.*, **31**, 193—196, 211—216).—Optically inactive cymene has not previously been obtained from oil of caraway in a pure condition,

the samples prepared invariably containing some terpene, or consisting of a mixture of two cymenes. In order to prepare a pure hydrocarbon, oil of caraway was distilled, and the fraction coming over at 165—225° collected apart and treated with sodium hydrogen sulphite and potassium hydroxide in order to remove cuminaldehyde. The oil was again distilled, when each fraction of higher boiling point was found to be less dextrorotatory than the one obtained immediately before it. For example, the 160—163° fraction had a rotatory power $[\alpha]_D = +22° 15'$, whilst the 174—176° fraction gave $[\alpha]_D = +3° 36'$. The latter, which appeared to be the purest, was fractionated several times, and finally a distillate, boiling constantly at 174—176°, and having a rotatory power $[\alpha]_D = +2·36°$, was obtained. This product, on redistillation, showed no further lowering of the dextrorotatory power.

In order to separate the terpene, which in all probability gave the hydrocarbon its optical activity, a cymene, having the rotatory power $[\alpha]_D = +8·41°$, was carefully dehydrated with calcium chloride, saturated with hydrogen chloride at −18°, and fractionally distilled under a reduced pressure of 50 mm. The 103—106° fraction thus obtained was then distilled under ordinary pressure, when a hydrocarbon boiling constantly at 175—177°, and giving a rotation of +1·17° in a 100 mm. tube, was obtained. On repeating the treatment with hydrogen chloride, a pure distillate was obtained, of the formula $C_{10}H_{14}$, which boiled constantly at 175—177°, and showed no rotatory power. The cymene prepared in this way is a clear, colourless liquid, having a pleasant odour quite distinct from that of *Ol. citri*. It boils constantly at 175—176·5°, and has a sp. gr. of 0·85957 at 15°, and 0·8585 at 20°. G. T. M.

Phenylacetylene Diiodide. By A. Peratoner (*Gazzetta*, **22**, ii, 65—85).—The author has attempted to prepare stereoisomeric phenylacetylene diiodides, but with the same lack of success as in the case of acetylene diiodide (Abstr., 1891, 654).

A mixture of phenylacetylene (2 grams) and iodine (5 grams) dissolved in glacial acetic acid, alcohol, carbon bisulphide, or concentrated potassium iodide solution (100 c.c.) after a time deposits a product which, when decolorised by sulphurous anhydride and crystallised from alcohol (50 per cent.) or dilute acetic acid, is found to be *phenylacetylene diiodide*, CPhI:CHI. It crystallises in almost colourless laminæ, melts at 76°, and gives off iodine at 150°; the molecular weight, determined by the cryoscopic method in acetic acid solution, is normal. It soon turns red on exposure to light, and can be distilled in a current of steam. The same substance is obtained on heating a solution of phenylacetylene (2 grams), iodine (5 grams), and iodic acid (10 grams) in absolute alcohol (20 c.c.) for 20 hours.

On oxidising phenylacetylene diiodide with chromic acid mixture, benzoic acid is formed. When treated with zinc dust in cold alcoholic solution, no appreciable action occurs, but on boiling for three hours in a reflux apparatus, complete reduction to phenylacetylene takes place. On heating the diiodide (5 grams) with mercuric chloride (10 grams)

and water (30 grams) for two hours in a closed tube at 110—120°, and eliminating the unchanged phenylacetylene diiodide by distilling the product in a current of steam, an oil is obtained which, after two repetitions of the above treatment, boils at 222°, and agrees in properties with the phenylacetylene dichloride, CPhCl:CHCl, described by Dyckerhoff (Abstr., 1878, 327, 481). Phenylacetylene diiodide has of course a similar constitution.

The author has endeavoured to prepare an isomeric diiodide by heating diiodocinnamic acid in a sealed tube at 120° with dilute hydrochloric acid (1 : 12). The product contained free iodine, and on distilling it in a current of steam, a little acetophenone volatilised and a brown resin was left. This, after repeated precipitations from its solution in benzene by light petroleum and subsequent crystallisation from ether, yielded triphenylbenzene.

On heating diiodocinnamic acid (10 grams) with water (160 c.c.) in sealed tubes at 140° for four to five hours, iodine and carbonic anhydride are liberated, and a mixture of acetone with crystals of the triiodocinnamene prepared by Liebermann and Sachse (Abstr., 1892, 470) is obtained. On heating the tubes at 110° for two hours, however, a mixture of unaltered diiodocinnamic acid and the phenylacetylene diodide described above is formed.

Action occurs when phenyliodacetylene, prepared by Liebermann and Sachse's method, is left in the cold for 24 hours in contact with concentrated hydriodic acid, or the mixture is heated for two hours on the water-bath. No product containing iodine could be isolated. On passing dry hydrogen iodide into a cooled solution of phenyliodacetylene (10 grams) in glacial acetic acid (100 c.c.) and leaving the product in sealed tubes for eight days, a satisfactory yield of the phenylacetylene diiodide described above is obtained. W. J. P.

Phenyliodacetylene. By A. Peratoner (*Gazzetta*, **22**, ii, 94—99).—Phenyliodacetylene, CPh:CI, boils at 134—138° under a pressure of 22 mm.; at 140° it becomes strongly coloured, and on cooling solidifies, owing to the formation of the diiodide. On treating it with hydrogen iodide in acetic acid solution, a product is obtained from which acetophenone is eliminated by distillation in a current of steam; the residue contains triphenylbenzene. It is slowly converted into a resin by exposure to sunlight. When shaken with aqueous alcoholic ammoniacal cuprous chloride solution in an atmosphere of hydrogen, a yellow precipitate is formed; this is collected, washed with water, and boiled with alcohol and ether. It has the composition CPh:C·Cu.

Phenyliodacetylene, when heated at 120° under 4 atmospheres pressure with zinc ethide and ether in an autoclave, yields a resinous product containing phenylethylacetylene. W. J. P.

Dinitrophenol [= 1 : 2 : 4]. By F. Reverdin and C. de la Harpe (*Chem. Centr.*, 1892, ii, 40; from *Arch. Sci. phys. nat. Geneva*, [3], **27**, 541—543).—400 grams of sulphuric acid, sp. gr. 1·82, is heated to 110°, 200 grams of phenol added, and the whole heated at 130—140° for five hours. The product is then poured into 600 c.c.

of water; 1375 grams of nitric acid, sp. gr. 1·2, is now added, the temperature not being allowed to exceed 40—50°, the whole is allowed to remain for 24 hours at the ordinary temperature, then heated from time to time on the water-bath during three days, and finally allowed to cool and filtered. The crystalline mass thus obtained is nearly pure dinitrophenol, and is rendered quite pure by twice boiling out with 2 litres of water. It melts at 114°, and, on reduction, yields the diamidophenol; this forms colouring matters when oxidised, or when its hydrochloride is heated with aromatic amines; the hydrochloride makes an indifferently good photographic developer. C. F. B.

Orthonitrobenzyl Alcohol. By C. Paal and A. Bodewig (*Ber.*, **25**, 2961—2966).—The best method of preparing orthonitrobenzyl alcohol, hitherto published, is that of Fischer, who obtained it by the action of alcoholic solutions of salts of organic acids on orthonitrobenzyl chloride and hydrolysis of the resulting salts. The reaction, however, is only quantitative when the mixture is heated in sealed tubes at 120°, which precludes the preparation of large quantities at once; if, however, the reaction is carried out in aqueous instead of alcoholic solution, it proceeds quantitatively at 100°, and the salts may, in this way, be readily prepared in any quantity.

Orthonitrobenzyl acetate, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OAc$, is obtained from orthonitrobenzyl chloride and concentrated aqueous sodium acetate, and crystallises from light petroleum or dilute alcohol in flat, white needles melting at 35—36°, and almost insoluble in water; the *benzoate*, $NO_2 \cdot C_6H_4 \cdot OBz$, obtained in a similar manner from sodium benzoate, crystallises from dilute alcohol in concentric aggregates of white needles, melts at 94°, is very slightly soluble in light petroleum, and insoluble in water. To obtain orthonitrobenzyl alcohol, the acetate is hydrolysed with moderately dilute sulphuric acid, or the benzoate with alcoholic potash, the latter giving the best results; it crystallises in slightly yellowish needles, and melts at 71—74°. When boiled with formic acid, it yields the *formate*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot O \cdot CHO$, which is an oil and could not be obtained pure.

The formate, acetate, and benzoate are readily reduced by zinc dust and hydrochloric acid with formation of the corresponding salts of orthamidobenzyl, which, however, very readily undergo hydrolysis, yielding orthamidobenzyl alcohol. The *formate*,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot O \cdot CHO,$$

is an unstable oil; the *acetate* crystallises in white needles; the *benzoate*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot OBz$, separates as an oil, which soon crystallises and yields a *hydrochloride*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot OBz, HCl$, crystallising from alcoholic ether in colourless prisms and melting at 143°; it is soluble in alcohol, insoluble in ether, and is dissociated by water.

Acidyl derivatives of orthamidobenzyl alcohol have also been prepared by Söderbaum and Widman (Abstr., 1889, 972), the acidyl group being in some cases combined with the nitrogen atom. These investigators endeavoured to convert the latter compounds into

derivatives of cumazone, $C_6H_4<\begin{matrix}N=CH\\ CH_2\cdot O\end{matrix}$ (Abstr., 1884, 302), but without success; the authors have made similar unsuccessful attempts to prepare cumazone derivatives from the acetate and benzoate; the formate yields, on distillation, water and an oil which soon partially crystallises; the crystals consist of *orthamidobenzyl alcohol*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot OH,$$

which, after recrystallisation from dilute alcohol, forms white plates melting at 82°. The examination of the basic oil is not yet completed, but it appears to consist chiefly of a cumazone derivative.

H. G. C.

Derivatives of Quinol, Resorcinol, and Phloroglucinol. By G. Ciamician and P. Silber (*Gazzetta*, **22**, ii, 56—64).—On passing dry chlorine into a cooled solution of dimethylquinol (3 grams) in glacial acetic acid (10 c.c.), much hydrogen chloride is evolved, and the liquid soon solidifies with formation of a dichlorodimethylquinol, which separates from alcohol in colourless prisms melting at 134°. This substance is probably identical with that obtained by Habermann (Abstr., 1879, 728), although the descriptions differ somewhat.

On passing dry chlorine into a solution of dimethylquinol (1 part) in glacial acetic acid (3 parts) without cooling, a mixture of tetrachlorodimethylquinol and chloranil separates. The former separates from an alcoholic solution of the mixture in crystals melting at 164°, not at 153—154° as stated by Habermann (*loc. cit.*). The mother liquor contains a *trichlorodimethylquinol*, which is obtained in minute, white needles melting at 91°, and is probably identical with the substance melting at 79° described by Habermann; it is isomeric with the compound prepared by the authors from cotoïn (compare Bartolotti, Abstr., 1892, 1315).

A solution of resorcinol (50 grams), potash (50 grams), and methyl iodide (130 grams) in methyl alcohol (150 c.c.), when heated in a reflux apparatus under a pressure of 250 mm. on the water-bath, yields an oil which has the composition of a dimethylresorcinol, and boils at 214—215° as stated by Habermann. It contains, however, far less methoxyl than is required by theory. A similar product is obtained on attempting to prepare the substance by the method given by Habermann (*loc. cit.*). A true dimethylresorcinol has, therefore, not yet been prepared.

The authors have previously shown that trimethylbenzoylphloroglucinol, when fused with potash, yields benzoic acid and trimethylphloroglucinol. When monobromotrimethylbenzoylphloroglucinol (2 grams) is distilled with powdered potash (15 grams), an oil is obtained which soon solidifies; this consists of *bromotrimethylphloroglucinol*. It separates from dilute alcohol in feathery needles, and melts at 96—97°.

W. J. P.

Isomeric Monobromanilines. By A. Nemiroffsky (*J. Russ. Chem. Soc.*, **22**, 482—488).—The author has carefully purified the

three isomeric monobromanilines, and made a comparative study of some of their properties.

Orthobromaniline crystallises in prisms melting at 29·6°. A litre of water at the ordinary temperature dissolves 2·169 grams.

$C_6H_4Br\cdot NH_2$ diss. + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 4·165 Cal. at 20°.

$C_6H_4Br\cdot NH_2$ diss. + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 6·827 Cal. at 19°.

$C_6H_4Br\cdot NH_2$ solid + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 1·931 Cal. at 19°.

From the last two equations, it follows that the heat of dissolution of solid orthobromaniline is −4·896 Cal. at 19°. 0·8313 gram of the hydrochloride was dissolved in 100 c.c. water at 20°; the heat of dissolution for this concentration and temperature was 4·160 Cal. When a solution of the hydrochloride (1 mol. in 2·5 litres water) is diluted repeatedly with 1 vol. of water, absorption of heat occurs on the first two dilutions amounting to −1·235 Cal. On further dilution, there is no appreciable absorption.

Metabromaniline forms needle-shaped crystals melting at 16·8°. At the ordinary temperature 1 litre of water dissolves 3·1928 grams.

$C_6H_4Br\cdot NH_2$ diss. + HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 5·788 Cal. at 20°.

$C_6H_4Br\cdot NH_2$ diss. + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 7·678 Cal. at 14°.

$C_6H_4Br\cdot NH_2$ solid + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 2·763 Cal. at 12°.

The heat of dissolution of solid metabromaniline at 12° is thus −4·895 Cal. The heat of dissolution of the liquid at 20° is −2·090 Cal., from which it follows that the heat of fusion is about −2·8 Cal. 8·1003 grams of the hydrochloride when dissolved in 400 c.c. water absorbed −3 807 Cal. at 19°. No absorption was noted on dilution.

Parabromaniline melts at 62°. 2·160 grams dissolves at the ordinary temperature in 1 litre of water.

$C_6H_4Br\cdot NH_2$ diss. + HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 6·531 Cal. at 19°.

$C_6H_4Br\cdot NH_2$ diss. + 2HCl diss. = $C_6H_4Br\,NH_2,HCl$ diss. + 7·058 Cal. at 19°.

$C_6H_4Br\cdot NH_2$ solid + 2HCl diss. = $C_6H_4Br\cdot NH_2,HCl$ diss. + 1·958 Cal. at 19°.

The heat of dissolution of the solid is, therefore, −5·1 Cal. at 19°.

10·1436 grams of the hydrochloride was dissolved in 400 c.c. water, the dissolution being accompanied by an absorption of 3·456 Cal. at 19°. Further dilution of the hydrochloride solution was not attended by absorption of heat.

From the thermochemical data given above, it would appear that the hydrochlorides of all the bromanilines are dissociated to a considerable extent into free base and hydrogen chloride when they are dissolved in water. J. W.

Action of Acetic Anhydride on Dimethylaniline. By F. Reverdin and C. de La Harpe (*Bull. Soc. Chim.* [3], **7**, 211—212).—When a mixture of acetic anhydride and dimethylaniline is exposed to the air, or, better, when air is blown through it, the liquid assumes a bluish tint, owing to the formation of tetramethyldiamidodiphenylmethane, of which as much as 10 per cent. may be obtained in a few days. Air is essential to the reaction, so that the strength of the standard solution of acetic anhydride in dimethylaniline used in the author's method of determining the relative amounts of aniline, methylaniline, and dimethylaniline in a mixture of those substances (Abstr., 1889, 1038) does not change if the solution is kept in full, well stoppered bottles. Jn. W.

Orthamidobenzyl Alcohol and its Derivatives. By C. Paal and E. Laudenheimer (*Ber.*, **25**, 2967—2973).—Friedländer and Henriques (Abstr., 1883, 187) have shown that orthamidobenzyl alcohol may be readily prepared by the reduction of orthonitrobenzyl alcohol with zinc dust and hydrochloric acid in alcoholic solution, and as the nitrobenzyl alcohol can now be obtained in quantity (see p. 20), the authors have investigated the properties of the amido-compound and its derivatives.

Orthamidobenzyl alcohol, when recrystallised, may be distilled with very slight decomposition at 270—280°, whilst under 5—10 mm. pressure, it distils unchanged at 160°; the impure compound, however, decomposes on heating. The *hydrochloride*, C_7H_9NO,HCl, forms white tablets melting at 108°, and readily soluble in alcohol; the *sulphate*, $(C_7H_9NO)_2H_2SO_4$, is a crystalline powder melting at 114°. It combines with almost all aldehydes with elimination of water, forming derivatives of the type $OH\cdot CH_2\cdot C_6H_4\cdot N:CHR$, which are for the most part crystalline compounds, stable towards alkalis, but resolved into their components by mineral acids. With the exception of acetone, no ketone reacts readily with the amido-alcohol even in presence of a dehydrating agent.

Ethylidine-orthamidobenzyl alcohol, $CHMe:N\cdot C_6H_4\cdot CH_2\cdot OH$, is obtained by the action of acetaldehyde on the amido-alcohol, and forms an oil which distils at 135—137° under a pressure of 5 mm.; *trichlorethylidine-orthamidobenzyl alcohol*, $CCl_3\cdot CH:N\cdot C_6H_4\cdot CH_2\cdot OH$, prepared in a similar manner from chloral, crystallises from dilute alcohol in white, lustrous plates melting at 92°. An *allylidene* derivative, $CH_2:CH\cdot CH(NH\cdot C_6H_4\cdot CH_2\cdot OH)_2$, is prepared by the action of acraldehyde on amidobenzyl alcohol in alcoholic solution; it is an amorphous, reddish powder; the authors give this formula with reserve, although the analytical figures are in accord with it. The *benzylidine* derivative, $CHPh:N\cdot C_6H_4\cdot CH_2\cdot OH$, forms white plates which are insoluble in water, and melts at 115°. The *metanitrobenzylidine*, *orthohydroxybenzylidine*, and *parahydroxybenzylidine* derivatives all form yellowish

needles, and melt at 93°, 117°, and 137° respectively. The *vanillidine* derivative, $OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, crystallises from alcohol in hemispherical aggregates of white needles, melts at 119°, and is extremely susceptible to the action of mineral acids; the *piperonidine* derivative, $CH_2{<}\overset{O}{O}{>}C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, forms stellate groups of white needles melting at 78°, and the *isopropylbenzylidine* derivative, $C_6H_4Pr^{\beta}{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, white plates melting at 103°.

Acetone, as already mentioned, combines very readily with orthamidobenzyl alcohol, and yields *isopropylene-orthamidobenzyl alcohol*, $CMe_2{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, which crystallises in large plates or flat needles, and melts at 120°. In small quantities, it distils at a high temperature unchanged, and, like the compounds obtained from the aldehydes, is stable towards alkalis, but is resolved into its components by mineral acids. H. G. C.

Methylphenylmercurammonium Hydroxide and Salts. By L. Pesci (*Gazzetta*, **22**, ii, 32—36).—*Methylphenylmercurammonium acetate*, NMePhHg·OAc, is obtained by adding a dilute alcoholic solution of methylaniline (2 mols.) to a concentrated alcoholic (50 per cent.) solution of mercuric acetate (1 mol.). The salt separates in brilliant, transparent laminæ, and is recrystallised from alcohol. It melts with decomposition at 149°, and is soluble in cold alcohol and acetic acid, but insoluble in ether and cold water. It is decomposed on boiling with water. On suspending it in water and adding potash, it yields the *hydroxide*, $NMePhHg{\cdot}OH,H_2O$, as colourless laminæ of pearly lustre, which lose their water of crystallisation over sulphuric acid. This substance melts at 118° and decomposes at 120°. It has an alkaline reaction and a caustic taste, is soluble in alcohol, sparingly so in cold water and insoluble in ether. It is decomposed by boiling with water, and on treatment with hydrogen sulphide, yields mercuric sulphide and salts of methylaniline. The *chloride* forms an amorphous, yellow powder, which, on exposure to light, turns green. It is insoluble in water and alcohol, decomposes at 108°, and has similar properties to the *bromide*, which decomposes at 120° yielding a violet product. The *nitrate* is obtained by the action of dilute nitric acid on the hydroxide; it forms colourless, hexagonal laminæ, and is very soluble in water, giving a solution which soon decomposes, and turns blue on heating; it is decomposed by alcohol and becomes green when kept. It decomposes at 150°, giving a brown product. The *hydrogen sulphate* is obtained in microscopic, transparent prisms, containing 1 mol. H_2O; it decomposes at 130° and is slowly converted into a greenish substance by the action of light. W. J. P.

Action of Carbonyl Chloride on Sodiophenylhydrazine. By A. Peratoner and G. Siringo (*Gazzetta*, **22**, ii, 99—105).—A diphenylurazine isomeric with that prepared by Pinner (*Ber.*, **21**, 2330) and Heller (Abstr., 1891, 1213) is obtained by the gradual addition of carbonyl chloride (15 grams) dissolved in benzene (45 grams) to sodiophenylhydrazine (40 grams) suspended in benzene

(150 grams). Heat is developed, and after 12 hours the liquid is filtered and the residue washed first with benzene and then with water. The urazine (10 grams) is repeatedly precipitated, first from its solution in glacial acetic acid by water, and finally from its chloroform solution by light petroleum; it forms white flocks, melts at 148—150°, and gives a normal molecular weight by the cryoscopic method in acetic acid solution. It is very soluble in alcohol and chloroform, sparingly so in benzene and insolub'e in water, ether, and light petroleum. On heating with acetic anhydride, it yields a *monacetyl* derivative as an amorphous, yellow powder which gives a normal molecular weight by the cryoscopic method.

The diphenylurazine described above is not identical with that obtained by Pinner (*loc. cit.*); the constitution of the latter not being known, it is impossible to say which of them is the symmetrical and which the unsymmetrical isomeride. W. J. P.

Action of Carbon Bisulphide on Orthamidobenzyl Alcohol. By C. PAAL and E. LAUDENHEIMER (*Ber.*, **25**, 2978—2980).—When carbon bisulphide is boiled with orthamidobenzyl alcohol in alcoholic solution, a reaction takes place similar to that occurring between carbon bisulphide and orthamidophenol. Whether the product has the formula $C_6H_4<\begin{matrix}NH\cdot CS\\ CH_2\cdot O\end{matrix}$, or the tautomeric formula $C_6H_4<\begin{matrix}N=C\cdot SH\\ CH_2\cdot O\end{matrix}$, has not yet been decided. The authors propose to term the substance *thiocumazone*, thus showing its connection with Widman's cumazonic acids (Abstr., 1884, 303).

Thiocumazone crystallises from dilute alcohol in white needles which are soluble in hot water and organic solvents and also in mineral acids and alkalis; it melts at 142° with evolution of hydrogen sulphide. The *platinochloride* forms yellow, amorphous flakes, and is insoluble in water and alcohol; the *potassium* salt, C_8H_6NSOK, crystallises in white plates having a satiny lustre, and deliquesces in the air. H. G. C.

Diphenylanilguanidine. By W. MARCKWALD and P. WOLFF (*Ber.*, **25**, 3116—3119).—Diphenylanilguanidine, $NHPh\cdot N:C(NHPh)_2$, or $NHPh\cdot C(NPh)\cdot NH\cdot NHPh$, is formed when either of the isomeric diphenylthiosemicarbazides (compare next abstract) is boiled with aniline (1 mol.) in alcoholic solution in presence of lead oxide; it is a colourless, crystalline powder, melts at 160°, turns reddish on exposure to the air, and is moderately easily soluble in benzene and toluene, but only sparingly in alcohol and ether. It is identical with the compound first obtained by L. Marckwald (*Inaug. Diss.*, Berlin, 1888) by the action of lead oxide on an alcoholic solution of diphenylthiocarbamide and phenylhydrazine, and also with that obtained by Wessel (Abstr., 1888, 1083) by heating phenylhydrazine with carbodiphenylimide; the melting point (138—139°) given by Marckwald is much too low, whereas that given by Wessel is about 44° too high. The *platinochloride*, $(C_{19}H_{18}N_4)_2,H_2PtCl_6$, is a yellowish-green compound, readily soluble in alcohol. The *picrate*, $C_{19}H_{18}N_4,C_6H_3N_3O_7$, crystallises in yellow needles, melts at 183° with decomposition, and

is readily soluble in alcohol, ether, and acetone, but only sparingly in benzene and toluene, and insoluble in water.

The *azo*-compound, $NHPh\cdot C(NPh)\cdot N_2Ph$, is obtained when an alcoholic solution of diphenylanilguanidine is boiled with precipitated mercuric oxide; it crystallises from dilute alcohol in lustrous, bright-red needles, melts at 111°, and is soluble in acids and most ordinary solvents, but insoluble in water.

A compound of the composition $C_{32}H_{28}N_6$ is formed with liberation of ammonia, benzene, and phenylhydrazine, when diphenylanilguanidine is heated at a moderately high temperature; it separates from boiling alcohol in the form of a colourless, crystalline powder, melts at 201°, and is only very sparingly soluble in all ordinary solvents. It is identical with the compound obtained by Wessel (*loc. cit.*) by heating diphenylanilguanidine with carbodiphenylimide. The *picrate*, $C_{32}H_{28}N_6,C_6H_3N_3O_7$, is a yellow, crystalline powder, melting at 240° with decomposition. F. S. K.

Stereoisomeric Thiosemicarbazides. By W. Marckwald (*Ber.*, **25**, 3098—3115; compare Dixon, Trans., 1892, 1012).—All the thiosemicarbazides which have been investigated, and which have been formed by the combination of fatty or aromatic thiocarbimides with phenylhydrazine, or with paratolylhydrazine, exist in two forms; the α-modification is less stable and melts at a lower temperature than the β-modification, into which it is converted when heated at a moderately high temperature, or when treated with hydrochloric acid. The behaviour of the two diphenylthiosemicarbazides is fully described below, and may be taken as correctly representing that of the other semicarbazides which show the same kind of isomerism.

Various thiocarbamides were examined, but were found to exist in only one form; symmetrical phenylparatolylthiocarbamide, for example, melts at 142°, whether prepared by the combination of paratolylthiocarbimide and aniline or by the combination of paratoluidine and phenylthiocarbimide. A number of thiosemicarbazides, prepared from asymmetrical substituted phenylhydrazines, were also examined, but in no case was the existence of two modifications observed.

The α- and β-modifications of the thiosemicarbazides are isomeric, as was proved, in the case of methylphenylthiosemicarbazide by molecular weight determinations in glacial acetic acid solution; they are, moreover, chemically, and not purely physically, isomeric, since, as is shown in the case of the diphenylthiosemicarbazides, they yield different additive products with methyl iodide. From the readiness with which the α-modifications of the thiosemicarbazides are converted into the corresponding β-forms, from the behaviour of the two diphenylthiosemicarbazides with methyl iodide, and with aniline and lead oxide (compare preceding abstract), and more especially from the study of the products obtained by treating the two diphenylthiosemicarbazides with carbonyl chloride, the author concludes that the two modifications are stereochemically isomeric; α-diphenylthiosemicarbazide may, therefore, be represented by the anti-configuration $\begin{matrix}SH\cdot C\cdot NHPh\\ \|\\ N\cdot NHPh\end{matrix}$, the β-modification by the syn-configuration

$$NHPh\cdot C(SH)\!:\!N\cdot NHPh$$

α-Diphenylthiosemicarbazide, prepared by treating phenylthiocarbimide with phenylhydrazine in well-cooled alcoholic solution, is only sparingly soluble in cold alcohol and benzene, but more readily in the hot solvents and in hot acetone. When heated in a capillary tube in the ordinary manner, it sinters at 139°, but does not melt until the temperature has risen to 176°; if, however, it is immediately heated at 139°, it liquefies completely, solidifies again a few seconds later, and then melts at 176°, having been converted into the β-modification; the true melting point of the α-modification is, therefore, 139°. Even after recrystallisation from solvents, it shows this peculiar behaviour on heating, but, after having once been liquefied, it shows no signs of melting until the temperature rises to 176°; it also crystallises unchanged from hot potash, but, on prolonged boiling with alcoholic potash, it is partially converted into the β-modification; on adding a trace of hydrochloric acid to its boiling alcoholic solution, it is completely converted into the isomeride.

β-Diphenylthiosemicarbazide is more sparingly soluble than the α-modification in all ordinary solvents, and melts at 176°; it crystallises from its solutions unchanged, and cannot be converted into the α-modification.

α-Phenylparatolylthiosemicarbazide, $C_7H_7\cdot NH\cdot C(SH)\!:\!N_2HPh$, prepared from paratolylthiocarbimide and phenylhydrazine in like manner, sinters at about 150°, being converted into the β-modification; it is only sparingly soluble in cold alcohol, acetone, and benzene, but more readily in the hot solvents. The β-modification melts at 176°, and is very sparingly soluble in benzene and only sparingly in hot acetone and alcohol.

α-Paratolylphenylthiosemicarbazide, $NHPh\cdot C(SH)\!:\!N_2H\cdot C_7H_7$, prepared from phenylthiocarbimide and paratolylhydrazine, melts at 123°, being converted into the β-modification; it is only sparingly soluble in cold, but readily in hot alcohol. The β-modification melts at 175°, and is more sparingly soluble than the isomeride.

α-Phenylmethylthiosemicarbazide, $NHMe\cdot C(SH)\!:\!N_2HPh$, obtained by the combination of methylthiocarbimide and phenylhydrazine (compare Dixon, Trans., 1890, 261), melts at 90—91°, is very readily soluble in cold acetone and glacial acetic acid, and moderately easily in cold alcohol and chloroform, but only sparingly in hot water; it is converted into the β-modification when heated at about 130°. The β-modification melts at 163—164°, and is readily soluble in cold acetone and glacial acetic acid, but more sparingly in alcohol and benzene.

A compound of the composition $C_{14}H_{16}N_3SI$ is formed when α-diphenylthiosemicarbazide is treated with methyl iodide in hot acetone solution; it crystallises from alcohol in colourless needles, melts at 164°, and is readily soluble in acetone and hot alcohol, but only very sparingly in benzene. The isomeride, $C_{14}H_{16}N_3SI$, obtained from β-diphenylthiosemicarbazide in like manner, forms colourless crystals, melts at 245°, and is more sparingly soluble than the α-compound.

When β-diphenylthiosemicarbazide is treated with carbonyl chloride in toluene solution, it is converted into the phenylanilidothiobiazolone described by Freund (Abstr., 1892, 508; 1890, 1440; 1888, 1187); this compound, contrary to Freund's statement, is not decomposed by an alkaline lead solution.

Phenylanilidothiobiazolone is also formed, together with an approximately equal quantity of diphenylimidobiazolonyl-μ-mercaptide, when α-diphenylthiosemicarbazide is gradually added to excess of a well-cooled toluene solution of carbonyl chloride; the two products can be separated by treatment with ammonia, in which phenylanilidothiobiazolone is insoluble.

Diphenylimidobiazolonyl-μ-mercaptide, $\begin{matrix}C(SH)\cdot NPh\\ \|\\ N\text{———}NPh\end{matrix}>CO$, is precipitated in crystals on acidifying the ammoniacal extract; it separates from hot alcohol in colourless crystals, melts at 219—221°, and is very readily soluble in hot alcohol and glacial acetic acid, but only sparingly in cold alcohol, ether, benzene, and chloroform, and insoluble in water. Molecular weight determinations gave results agreeing with those required for the molecular formula given above. It has a distinctly acid character, and its solution in ammonia gives, with many salts of the heavy metals, insoluble compounds, which are stable towards dilute mineral acids; lead acetate, for example, yields a light-yellow, crystalline compound, copper sulphate a dirty-green, amorphous precipitate, and silver nitrate a colourless, amorphous compound of the composition $C_{14}H_{10}N_3OSAg$.

Diphenylimidobiazolonyl-μ-methyl sulphide hydriodide,

$$(C_{15}H_{13}N_3OS)_2,HI,$$

is slowly deposited in yellowish crystals when the preceding compound is treated with methyl iodide in alcoholic or chloroform solution at the ordinary temperature; it melts at 155—156°, and is very readily soluble in hot water, but only sparingly in alcohol and cold water, and very sparingly in ether and chloroform. The *base*, $C_{15}H_{13}N_3OS$, prepared by decomposing an aqueous solution of the salt with concentrated potassium carbonate, crystallises from hot water, melts at 185°, and is very readily soluble in hot water, cold alcohol, ether, chloroform, and glacial acetic acid; its molecular weight was determined in glacial acetic acid and in benzene solutions, with results which showed that it has the molecular formula given above; it is decomposed by hot alkalis with liberation of methyl mercaptan. The *platinochloride*, $(C_{15}H_{13}N_3OS)_4,H_2PtCl_6$, crystallises from hot water in orange-red prisms, melts at 186° with decomposition, and is only sparingly soluble in cold water and alcohol, but moderately easily in the hot solvents.

Diphenylimidobiazolone, $\begin{matrix}CH\cdot NPh\\ \|\\ N\text{—}NPh\end{matrix}>CO$, is produced when diphenylimidobiazolonyl-μ-mercaptide is oxidised with the theoretical quantity of hydrogen peroxide in sodium carbonate solution; it crystallises from alcohol in colourless needles, melts at 249°, and is very readily soluble in cold glacial acetic acid, but only very sparingly in ether,

benzene, and alcohol, and insoluble in water and sodium carbonate; it crystallises unchanged from dilute mineral acids, and is not decomposed by boiling alkalis. Molecular weight determinations gave results in accordance with those required by a compound of the molecular formula given above.

Triphenylthiosemicarbazide, $NHPh{\cdot}CS{\cdot}NH{\cdot}NPh_2$, is formed when asymmetrical diphenylhydrazine is treated with phenylthiocarbimide in alcoholic solution; it melts at 181°, decomposes at a higher temperature, and is readily soluble in hot glacial acetic acid, but only sparingly in ether, alcohol, and cold glacial acetic acid.

Diphenylmethylthiosemicarbazide, $NHMe{\cdot}CS{\cdot}NH{\cdot}NPh_2$, prepared from methylthiocarbimide and asymmetrical diphenylhydrazine, melts at 203—204°, and is only sparingly soluble in ether, cold alcohol, and glacial acetic acid, but moderately easily in hot alcohol and hot glacial acetic acid.

Diphenylallylthiosemicarbazide melts at 108°, not at 103°, as stated by Michaelis and Claesson (Abstr., 18-9, 1161).

Diphenylmethylthiosemicarbazide, $NHPh{\cdot}CS{\cdot}NH{\cdot}NMePh$, prepared from phenylthiocarbimide and asymmetrical methylphenylhydrazine, melts at 154°, as stated by Fischer.

Dimethylphenylthiosemicarbazide, $NHMe{\cdot}CS{\cdot}NH{\cdot}NMePh$, obtained by the combination of methylthiocarbimide and asymmetrical methylphenylhydrazine, crystallises in lustrous plates, melts at 162·5°, and is very readily soluble in hot alcohol, benzene, and glacial acetic acid, but only sparingly in cold ether.

Diphenylmethylthiosemicarbazide, $NHPh{\cdot}CS{\cdot}NMe{\cdot}NHPh$, is readily obtained by treating phenylthiocarbimide with symmetrical methylphenylhydrazine in alcoholic solution; it crystallises in colourless needles, melts at 175°, and is only sparingly soluble in cold alcohol and ether, but very readily in hot alcohol and benzene.

Triphenylthiosemicarbazide, $NHPh{\cdot}CS{\cdot}NPh{\cdot}NHPh$, is formed when hydrazobenzene is boiled for a long time with phenylthiocarbimide in alcoholic solution; it melts at 173—174°, and dissolves freely in boiling benzene, toluene, and glacial acetic acid, but is only sparingly soluble in hot alcohol and ether; it does not combine with phenylthiocarbimide in boiling alcoholic solution, a fact which proves that it cannot be a benzidine derivative of the constitution

$$NHPh{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2.$$

F. S. K.

Dibenzamide and Tribenzamide. By M. Jaffé (*Ber.*, **25**, 3120—3121).—In the preparation of benzamide by the action of ammonium carbonate on benzoic chloride, small quantities of dibenzamide and tribenzamide are formed, and remain undissolved on treating the product with boiling water; on recrystallising the residue from hot alcohol, tribenzamide is deposited in slender, colourless needles melting at 201—202° (corr.), and identical with the compound described by Curtius (Abstr., 1891, 58); the alcoholic mother liquors yield, on evaporation, a small quantity of dibenzamide, which, after recrystallisation from hot water, is obtained in colourless needles melting at 147°. The sum of the weights of the dibenzamide

and tribenzamide never exceeds 5 per cent. of the benzoic chloride employed, even when the method of preparation is altered; it is also immaterial whether commercial benzoic chloride, or a sample prepared from pure benzoic acid, is employed. F. S. K.

Seleno- and Thio derivatives of Ethylamine. By W. MICHELS (*Ber.*, **25**, 3048—3055).—Dibenzamidodimethyl diselenide does not react with phosphoric chloride in an analogous manner to the bisulphide (Abstr., 1891, 817), but gives rise to μ-phenyloxazoline. *μ-Methylselenazoline*, $\begin{matrix}CH_2\cdot Se\\ |\\ CH_2\cdot N\end{matrix}\!\!>\!CMe$, is obtained by heating a mixture of diamidodiethyl diselenide hydrochloride (1·6 grams), sodium acetate (0·9 gram), and acetic anhydride (3·9 grams) on the water-bath in a reflux apparatus for half an hour, adding phosphoric chloride (3·2 grams), and continuing the heating for a quarter of an hour. The product is rendered alkaline and distilled with steam; on adding alkali to the distillate, an oil separates which is extracted with ether. It boils at 160—162° (752·2 mm.), has a specific gravity above 1·5, and an index of refraction $n_D = 1·556$ at 20°. The *picrate* melts at 158—159°.

Phthalimidoethylbenzyl sulphide, $C_6H_4O_2{:}N\cdot C_2H_4\cdot S\cdot CH_2Ph$, is formed when ethylmercaptophthalimide (Gabriel, Abstr., 1891, 815) is dissolved in absolute alcohol (2 parts), and an alcoholic solution of sodium ethoxide (1 mol.), and subsequently benzyl chloride, are gradually added with cooling; on pouring the product into water, the compound is precipitated; it crystallises from methyl alcohol in white leaflets, and melts at 76—78°. When it is dissolved in 10 per cent. potash, and hydrochloric acid added to the solution, *benzylthioethylphthalamic acid*, $CH_2Ph\cdot S\cdot C_2H_4\cdot CO\cdot C_6H_4\cdot COOH$, separates; and this, on being heated in a reflux apparatus with concentrated hydrochloric acid (100 parts), yields phthalic acid and benzylthioethylamine hydrochloride. The *base* of the last-named salt, $CH_2Ph\cdot S\cdot C_2H_4\cdot NH_2$, is a colourless oil of an unpleasant odour and a biting taste, boils at 270—272° (754·5 mm.), is very unstable, and absorbs carbonic anhydride from the air. The *picrate* melts at 125—127°; the *platinochloride* is a pale yellow, crystalline powder. The *benzoyl* derivative melts at 78—80°; when heated on the water-bath with phosphoric chloride, benzyl chloride passes over, and the residue, on being rendered alkaline and distilled in a current of steam, yields μ-phenylthiazoline. When an alcoholic solution of phthalimidoethylbenzyl sulphide is gently warmed with bromine water, the *sulphoxide*, $C_6H_4O_2{:}N\cdot C_2H_4\cdot SO\cdot CH_2Ph$, which melts at 143—145°, separates in lustrous, white tables; whilst if the sulphide (3 mols.) is dissolved in 80 per cent. acetic acid, and warmed with a solution of chromic acid (4 mols.) in dilute acetic acid, the *sulphone*, $C_6H_4O_2{:}N\cdot C_2H_4\cdot SO_2\cdot CH_2Ph$, is obtained; this crystallises from alcohol in white leaflets, melts at 137—139°, and decomposes into phthalic acid and benzyl chloride when heated in a sealed tube at 160°.

Phthalimidoethylbenzomercaptal, $CHPh(S\cdot C_2H_4\cdot N{:}C_6H_4O_2)_2$, produced by heating phthalimidoethyl mercaptan with an excess of benz-

aldehyde in a current of hydrogen chloride at 100°, forms small prisms, melts at 155—156°, and is sparingly soluble in alcohol, but more readily in glacial acetic acid. When heated with 10 per cent. alkali, the phthalamic acid is precipitated on adding dilute acid to the solution; the precipitate, if heated in a reflux apparatus for two hours with 25 per cent. hydrochloric acid, yields phthalic acid and *amidoethylbenzmercaptal hydrochloride*, $CHPh(S{\cdot}C_2H_4{\cdot}NH_2)_2,2HCl$, melting at 195°.

Acetone phthalimidoethylmercaptal, $CMe_2(S{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2)_2$, obtained from phthalimidoethyl mercaptan and acetone, crystallises in small tablets, melts at 141—143°, and, when heated with hydrochloric acid, yields acetone, phthalic acid, and amidomercaptan.

Phthalimidoethylformomercaptal, $CH_2(S{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2)_2$, is formed by heating on the water-bath phthalimidoethyl mercaptan (10 grams), dissolved in absolute alcohol (20 c.c.), with a 5 per cent. solution of sodium ethoxide (22 c.c.) and methylene chloride (4 grams). It separates from glacial acetic acid in small, colourless crystals, melts at 133—134°, and, when heated with fuming hydrochloric acid (10 parts) at 180°, yields phthalic acid and *amidoethylformomercaptal hydrochloride*, $CH_2(S{\cdot}C_2H_4{\cdot}NH_2)_2,2HCl$, melting at 186—187°; the free *base* of the last-named salt is fairly soluble in water, and the *picrate* melts at 139—141°. A. R. L.

Triamidopropane. By S. Gabriel and W. Michels (*Ber.*, **25**, 3056—3058).—*β-Chlorotrimethylenediphthalimide*,

$$CHCl(CH_2{\cdot}N{:}C_8H_4O_2)_2,$$

is obtained by adding phosphoric chloride (7 grams) to finely pulverised β-hydroxytrimethylenediphthalimide (10 grams) suspended in boiling benzene (50 c.c.), and heating the mixture for a quarter of an hour; the compound is then collected and washed with benzene and aqueous alcohol. When crystallised from 70 per cent. acetic acid, it forms slightly-coloured, thick prisms, and melts at 208—209°. If it is heated in a sealed tube with fuming hydrochloric acid (10 parts) at 180—200° for four hours, and the eliminated phthalic acid filtered off, the filtrate, on evaporation to dryness, yields a residue of *β-chlorotrimethylenediamine hydrochloride*,

$$NH_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}NH_2,2HCl,$$

which crystallises from alcohol in lustrous, white leaflets, and melts at 216°; the *picrate* melts at 214°; and the free *base*, which is very soluble in water, is precipitated from solutions of its salts by concentrated alkalis as a colourless oil.

Triphthalimidopropane, $C_8H_4O_2{:}N{\cdot}CH(CH_2{\cdot}N{:}C_8H_4O_2)_2$, is formed by heating an intimate mixture of potassium phthalimide (1 part) and β-chlorotrimethylenediphthalimide (2 parts) at 215—225°. The pulverised product is digested with 5 per cent. sodium hydroxide for half an hour, collected, and washed with water. The compound crystallises from glacial acetic acid in reddish needles, and melts at 226—227°. On heating it with hydrochloric acid at 100°, phthalic acid, ammonia, and a substance having the odour of pyridine were recognised, but apparently the expected triamidopropane was not present.

A. R. L.

Mesitylene. By S. LANDAU (*Ber.*, **25**, 3011—3018).—*ω-Mesityl-phthalimide*, $C_6H_3Me_2\cdot CH_2\cdot N:C_8H_4O_2$, is obtained by heating a mixture of equal weights of mesityl bromide, $C_6H_3Me_2\cdot CH_2Br$, and potassium phthalimide at 220° for half an hour and then at 235° for two hours. The product is powdered, extracted with water, then with dilute sodium hydroxide, and crystallised from acetic acid. It forms white needles, melts at 157°, and is easily soluble in alcohol and hot acetic acid, more sparingly in ether, benzene, and chloroform.

ω-Mesitylphthalamic acid, $C_6H_3Me_2\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot COOH$, is obtained by warming the preceding compound on the water-bath with 10 per cent. potassium hydroxide until it dissolves, and then precipitating with hydrochloric acid. It crystallises from dilute alcohol or benzene in slender needles, melts at 152°, is insoluble in hot water, and easily soluble in alcohol and acetic acid, more sparingly in benzene. The *silver salt* is a white, crystalline precipitate, and decomposes above 182°. The acid is only very slightly decomposed by boiling with concentrated hydrochloric acid in a reflux apparatus for three hours.

ω-Mesitylamine, $C_6H_3Me_2\cdot CH_2\cdot NH_2$, is obtained by heating mesitylphthalimide with concentrated hydrochloric acid (5 parts) in a sealed tube at 190—200° for six hours. It is a colourless liquid, has a strong odour of herring brine, boils at 217—218° under 756 mm. pressure without decomposition, and eagerly absorbs carbonic anhydride from the air. The *hydrochloride* crystallises in four-sided prisms, and melts at 224°. The *nitrate* crystallises in long, white needles. The *picrate* forms yellow, rhombic crystals, and melts at 225° with decomposition. The *platinochloride* crystallises in golden-yellow, six-sided leaflets, and melts at 204°. The *acetyl compound* crystallises from dilute alcohol and acetic acid in needles, and melts at 78°. The *benzoyl compound* crystallises from alcohol in aggregates of white needles, melts at 78°, and is easily soluble in alcohol, benzene, and acetic acid.

ω-Mesitylcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_3Me_2$, is obtained by warming an aqueous solution of mesitylamine hydrochloride with potassium cyanate. It crystallises from alcohol in silvery leaflets, and melts at 181°.

ω-Mesitylthiocarbamide, $NH_2\cdot CS\cdot NH\cdot CH_2\cdot C_6H_3Me_2$, is obtained by warming an aqueous solution of mesitylamine hydrochloride and potassium thiocyanate on the water-bath. It crystallises from water in slender, white needles, turns yellow on exposure to air, melts at 135°, and is easily soluble in alcohol and acetic acid.

Dimesitylthiocarbamide, $CS(NH\cdot CH_2\cdot C_6H_3Me_2)_2$, is obtained by adding a slight excess of carbon bisulphide to an alcoholic solution of mesitylamine; it crystallises from alcohol in long, thin needles, and melts at 165°.

Allylmesitylthiocarbamide, obtained by gradually adding allylthiocarbimide to mesitylamine, crystallises from alcohol in white needles, melts at 91°, and is sparingly soluble in water, easily so in alcohol.

Dinitromesitylacetamide, $C_6HMe_2(NO_2)_2\cdot CH_2\cdot NHAc$, is obtained by

gradually adding mesitylacetamide to 4—5 times the quantity of fuming nitric acid cooled with ice. It crystallises from dilute alcohol in long, thin, pale yellow prisms, melts at 162°, and is easily soluble in alcohol, acetic acid, and mineral acids, sparingly in cold water.

Dinitromesitylamine is obtained by heating the preceding acetyl compound with hydrochloric acid in a sealed tube at 150°, and is a brown, odourless liquid which easily decomposes. The *hydrochloride* crystallises in leaflets, melts at 245° with decomposition, and is easily soluble in water, sparingly so in concentrated hydrochloric acid and absolute alcohol. The *picrate* crystallises from water in long, bright yellow prisms, decomposes at 220°, and is insoluble in alcohol. The *platinochloride* crystallises from water in golden-yellow leaflets.

ω_2-Diphthalimidomesitylene, $C_6H_3Me(CH_2\cdot N{:}C_8H_4O_2)_2$, is obtained by heating a mixture of dibromo- or dichloro-mesitylene with potassium phthalimide (2 mols.) at 220—240° for about half an hour. The product is crystallised from nitrobenzene, and dried on porous plates. It crystallises from acetic acid in brownish needles, melts at 244°, and is insoluble in alcohol.

Mesitylenediphthalamic acid, $C_6H_3Me\cdot(CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot COOH)_2$, is obtained by boiling the preceding compound with alcoholic potash until it dissolves. It separates in white prisms on adding hydrochloric acid to the dilute ammoniacal solution, melts at 187°, and is easily soluble in alcohol and acetic acid, sparingly so in water.

ω_2-Diamidomesitylene, $C_6H_3Me(CH_2\cdot NH_2)_2$, is obtained by heating the diphthalyl compound in a sealed tube with hydrochloric acid at 200—220° for some hours. It is a colourless liquid, having a strong ammoniacal odour, boils at 268°, eagerly absorbs carbonic anhydride from the air, and yields well crystallised salts with acids. The *picrate* crystallises in small, bright yellow needles, and decomposes at 235°. The *platinochloride* crystallises in yellow plates, and decomposes at 258°. The *diacetyl* compound crystallises from chloroform in white needles, melts at 165°, and is easily soluble in hot water, concentrated hydrochloric acid, benzene, and chloroform, and yields a well crystallised platinochloride. E. C. R.

Hydrobenzoic Acids. By O. Aschan (*Annalen*, **271**, 231—284).—In this paper, the author gives a complete account of his work on the reduction products of benzoic acid, and corrects some of the statements made in earlier papers (compare Abstr., 1891, 1053 and 1481); only the new facts are given in this abstract.

In preparing Δ^2-tetrahydrobenzoic acid by the method already described, hydrobenzoïn (m. p. 134°) is formed in small quantities, as well as benzyl alcohol.

Δ^2-Tetrahydrobenzoic acid can be distilled in an atmosphere of carbonic anhydride, and then boils at 234—235° (mercury entirely in vapour) with very slight decomposition, yielding traces of a neutral liquid, which is probably the lactone of γ-hydroxyhexahydrobenzoic acid. The acid is only sparingly soluble (1·34 grams in 100 c.c.) in water at 20°, and is readily oxidised to benzoic acid on exposure to the air; its electrical conductivity is $K = 0{\cdot}00305$. The *calcium* salt, $(C_7H_9O_2)_2Ca$, crystallises in needles, and is moderately easily soluble

in cold water, but more sparingly in alcohol. The *silver* salt, $C_7H_9O_2Ag$, is only very sparingly soluble in boiling water, by which it is decomposed; it is very sensitive to light. The *methyl* salt boils at 188—189° (mercury entirely in vapour), and has a sp. gr. of 1·0433 at 20°/20°; it combines readily with bromine in ethereal solution yielding an oil. Δ^2-Tetrahydrobenzoic acid is identical with the benzoleïc acid obtained by Herrmann by reducing benzoic acid with sodium amalgam in acid solution (*Annalen*, **132**, 75).

γ-Hydroxyhexahydrobromobenzoic lactone, $CH_2<\begin{matrix}CH_2\cdot CH\\CH_2\cdot CH\end{matrix}>\begin{matrix}CO\\CHBr\end{matrix}>O$, is easily obtained by warming the dibromo-additive product of the Δ^2-tetrahydro-acid with sodium carbonate; it crystallises from dilute alcohol in long, flat prisms, melts at 67°, and is readily soluble in benzene, ether, alcohol, and glacial acetic acid, but only sparingly in water; it is decomposed by alcoholic potash in the cold with formation of potassium bromide, and a substance which is readily soluble in water, and which decolorises potassium permanganate.

γ-Ethoxy-Δ^1-tetrahydrobenzoic acid, $C_9H_{14}O_3$, not a dihydrobenzoic acid as at first supposed (Abstr., 1891, 1482), is formed when the dibromo-additive product of the Δ^2-tetrahydro-acid is treated with alcoholic potash at the ordinary temperature; it crystallises from water in long, transparent prisms, melts at 73°, and is very readily soluble in all ordinary solvents except water; it is immediately oxidised by potassium permanganate in sodium carbonate solution. Its salts are readily soluble and badly characterised. The *silver* salt, $C_9H_{13}O_3Ag$, melts at 130—140° when quickly heated, and is stable in the light. The *dibromo*-additive product, $C_9H_{14}Br_2O_3$, is formed, when the acid is treated with bromine in chloroform solution in the dark; it crystallises from a mixture of benzene and light petroleum in large, flat prisms, melts at 125—126°, and decolorises an alkaline solution of potassium permanganate only after long keeping; its *sodium* salt is only very sparingly soluble in water, from which it crystallises in octagonal prisms. When ethoxy-Δ^1-tetrahydrobenzoic acid is heated with a saturated glacial acetic acid solution of hydrogen bromide at 100° for 12 hours, it is converted into the dibromohexahydrobenzoic acid (m. p. 166°) previously described.

Hexahydrobenzoic acid (m. p. 28°) can not only be obtained by reducing the mixture of hydrobromo-additive products of the Δ^2-tetrahydro-acid with sodium amalgam (*loc. cit.*), but also by heating the Δ^2-tetrahydro-acid with concentrated hydriodic acid at 200°. It boils at 232—233° (mercury entirely in vapour), has a disagreeable smell and is very readily soluble in alcohol and ether, but only moderately easily in water; attempts to convert the acid into a stereochemical isomeride were unsuccessful, as was expected. The *silver* salt, $C_7H_{11}O_2Ag$, is a microcrystalline compound, sparingly soluble in boiling water. The methyl salt boils at 179—180° (mercury entirely in vapour). The *ethyl* salt, $C_6H_{11}\cdot COOEt$, is a mobile oil, of sp. gr. 0·9723 at 4°/4° and 0·93624 at 20°/4°; it boils at 194·5—195·5° (mercury entirely in vapour).

Δ^1-Tetrahydrobenzoic acid melts at 29°, and is only sparingly soluble (0·7 gram in 100) in water at 20°; its sp. gr. is 1·1089

at 20°/20°, and its electrical conductivity $K = 0{\cdot}00221$. Its salts are more stable and more sparingly soluble than those of the Δ^2-tetrahydro-acid. The *silver* salt, $C_7H_9O_2Ag$, crystallises in prisms. The *calcium* salt crystallises in colourless prisms with 1 mol. H_2O, the *ammonium* salt in lustrous plates. The *methyl* salt, $C_6H_9{\cdot}COOMe$, is a colourless liquid of sp. gr. 1·05607 at 4°/4°, and 1·04183 at 20°/4°; it boils at 193·5—194·5° (mercury entirely in vapour).

β-Bromohexahydrobenzoic acid, $C_6H_{11}Br{\cdot}COOH$, is formed, when the Δ^1-tetrahydro-acid is heated with a saturated glacial acetic acid solution of hydrogen bromide at 100° for 4—5 hours; it crystallises from hot formic acid in large, flat, seemingly rhombic prisms or plates, melts at 108—109°, and decolorises an alkaline solution of potassium permanganate; when boiled with dilute sodium carbonate, it is reconverted into the Δ^1-tetrahydro-acid.

When the dibromo-additive product of the Δ^1-tetrahydro-acid is treated with alcoholic potash, it yields an acid which is much more readily soluble in water, and less stable than the Δ^1-tetrahydro-acid; this product resinifies on keeping, and is probably a dihydro-acid.

A dihydroxyhexahydrobenzoic acid seems to be formed when dibromohexahydrobenzoic acid is dissolved in dilute sodium carbonate ($\frac{1}{2}$ mol.), and the solution then boiled; a small quantity of a neutral oil separates from the solution, but the principal product is an acid which is best isolated in the form of its calcium salt. This compound crystallises from water in large, transparent plates, is almost insoluble in cold water, and has the composition $[C_6H_9(OH)_2{\cdot}COO]_2Ca + 2H_2O$; the acid, prepared from the calcium salt, is very hygroscopic, and reduces ammoniacal silver nitrate solution on boiling.

Diacetoxyhexahydrobenzoic acid, $C_6H_9(OAc)_2{\cdot}COOH + H_2O$, is obtained when the calcium salt just described is treated with acetic chloride, and the product recrystallised from water; it forms small, monosymmetric crystals, $a : \breve{b} : c = 3{\cdot}4176 : 1 : 1{\cdot}1541$, $\beta = 86°\ 51'$, melts at 72—73°, and loses water when kept over sulphuric acid, being converted into a syrup, which crystallises again on treatment with water; it is readily soluble in alcohol, but more sparingly in cold water. The *silver* salt crystallises in long, slender needles, and is moderately stable in the light. F. S. K.

Organic Sulphur Compounds. By A. Delisle and A. Schwalm (*Ber.*, **25**, 2980—2984; compare Abstr., 1889, 488).—*β-Thioparatolylpropionic acid*, $C_6H_4Me{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is obtained quantitatively by boiling ethyl β-iodopropionate with the sodium derivative of parathiocresol in molecular proportion, and hydrolysing the ethyl salt thus formed with alcoholic potash; it crystallises from light petroleum in lustrous plates, and melts at 70—71°. It separates from ether in large, transparent, monosymmetric or asymmetric tablets, and is soluble in most organic solvents. The *silver* salt, $C_{10}H_{11}SO_2Ag$, crystallises from hot water in broad, transparent needles which are fairly stable towards light; the *calcium* salt, $(C_{10}H_{11}SO_2)_2Ca + 3H_2O$, forms white, hair-like needles, and the *barium* salt, $(C_{10}H_{11}SO_2)_2Ba + 2H_2O$, lustrous plates. The *ethyl* salt, obtained in the manner described above, is a thick, yellowish liquid, and boils at 171° under 12 mm. pressure.

α-Hydroxy-β-thiotolylisobutyric acid,

$$C_6H_4Me\cdot S\cdot CH_2\cdot CMe(OH)\cdot COOH,$$

is prepared by the action of hydrogen cyanide on thiotolylacetone, $C_6H_4Me\cdot S\cdot CH_2\cdot COMe$, and hydrolysis of the nitrile thus formed; it crystallises from hot water containing hydrochloric acid in silky, flexible needles, and melts at 101—102°. The *calcium* salt crystallises in stellate groups of needles, and the *barium* salt in white plates; the *silver* salt forms a white, curdy precipitate.

The authors have also prepared the ethyl phenylthioacetate (ethyl thiophenylacetoacetate) described by Otto and Rössing, the existence of which has frequently been denied; it is readily obtained by the action of sodium phenylmercaptide on ethyl chloracetoacetate, and is a yellow oil which decomposes at 60—70° with formation of phenyl bisulphide, a reaction which takes place slowly at the ordinary temperature.

Ethyl metethoxyphenylthioacetoacetate, $CHAc\cdot S\cdot C_6H_4(OEt)\cdot COOEt$, is obtained by the action of the sodium compound of metethoxyphenyl hydrosulphide (Abstr., 1891,310) on ethyl chloracetoacetate, and is a pale yellow oil, which, like the preceding compound, readily decomposes with formation of the corresponding bisulphide. *Metethoxyphenyl bisulphide*, $S_2(C_6H_4\cdot OEt)_2$, forms compact crystals melting at 42—43°, and may also be obtained by the action of iodine on the hydrosulphide.

β-Thiotolyllevulinic acid, $CHAc\cdot S(C_6H_4Me)\cdot CH_2\cdot CH_2\cdot COOH$, is prepared by the action of the sodium derivative of parathiocresol on ethyl β-bromolevulinate, and hydrolysis of the ethyl salt; it melts at 103—104°, and yields a *hydrazone* melting at 120—121°. The *barium* salt, $(C_{12}H_{13}O_3S)_2Ba$, crystallises in white, concentric groups of needles. H. G. C.

Phenylpyruvic Acid and Phenylglycidic Acid. By E. Erlenmeyer, Jun. (*Annalen*, **271**, 137—180).—In the first part of this paper, the author describes experiments by which he claims to have proved that Glaser's "phenylhydroxyacrylic acid" is, in reality, phenylglycidic acid, identical with the compound obtained by Plöchl by treating phenyl-β-bromolactic acid with potash, and considered by him to be α-hydroxycinnamic acid. In the second part of the paper, it is shown that the acid obtained by Plöchl from the condensation product of benzaldehyde and hippuric acid (Abstr., 1884, 604) is identical with phenylpyruvic acid.

When the sodium salt of phenylglycidic acid (Glaser's "phenylhydroxyacrylic acid") is covered with ether and treated with dry hydrogen chloride, sodium chloride is deposited, and phenyl-β-chlorolactic acid remains in solution; on fractionally precipitating, with light petroleum, the ethereal solution, previously freed from hydrogen chloride by keeping over potash, the phenyl-β-chlorolactic acid is obtained as an almost colourless oil which soon solidifies. It separates from hot chloroform in small, slender needles, melts at 141—142° with decomposition, and is identical with the acid obtained by Leschhorn (*Inaug. Diss., Würzburg*, 1884), by the action of hydrochloric

acid on phenylglyceric acid; when treated with excess of soda at the ordinary temperature, it is converted into sodium phenylglycidate.

An *acid* of the composition $C_9H_{11}NO_3$ is formed when sodium phenylglycidate ("sodium phenylhydroxyacrylate") is treated with concentrated ammonia at the ordinary temperature, and the product decomposed with acetic acid; it decomposes at 220—221°, and is probably a *phenyl-β-amidolactic acid* of the constitution

$$NH_2{\cdot}CHPh{\cdot}CH(OH){\cdot}COOH.$$

The *acid* of the composition $C_{14}H_{19}NO_3$, obtained from sodium phenylglycidate and piperidine in like manner, decomposes at 244°.

Sodium phenylanilidolactate, $C_{15}H_{14}NO_3Na$, can be prepared by treating an aqueous solution of sodium phenylglycidate with aniline, and recrystallising the product from hot alcohol; when treated with dilute acetic acid, it yields phenylanilidolactic acid, melting at 144—145°.

Phenylglycidic acid can be obtained by adding benzaldehyde and a few drops of alcohol to an ethereal solution of ethyl chloracetate containing sodium in suspension.

Ethyl phenylcyanopyruvate, CN·CHPh·CO·COOEt, is formed when benzyl cyanide is treated with ethyl oxalate and sodium ethoxide in alcoholic solution and the product decomposed with water. It is a crystalline substance, melts at 130° and is soluble in alcohol, soda, ammonia, and sodium carbonate; in its alcoholic solution, ferric chloride produces a dark green coloration; it is readily decomposed by alkalis, yielding benzyl cyanide, but when boiled with moderately concentrated sulphuric acid, it gives phenylpyruvic acid.

F. S. K.

Action of Sulphuric Acid on Quinol. By J. H. Stebbins, Jun. (*Chem. Centr.*, 1892, ii, 40—41; from *J. Amer. Chem. Soc.*, **13**, 155).—Since the utility of quinol as a photographic developer is considerably impaired by its slight solubility in water, the author has prepared its more soluble sulphonic derivative, $C_6H_3(OH)_2{\cdot}SO_3H$, which he has found to act satisfactorily as a developer. It is prepared by heating 10 grams of quinol with 20 grams of sulphuric acid, sp. gr. 1·82, freeing the solid mass from sulphuric acid by means of porous plates and filter paper, and crystallising from a small quantity of alcohol in a vacuum. In forms long, brownish, transparent, rhombic prisms, containing alcohol of crystallisation. Its salts oxidise readily in the air. The barium salt, probably $(C_6H_5O_5S)_2Ba + H_2O$, is most easily prepared; it forms small, white, hexagonal prisms, soluble in cold water and dilute alcohol, and giving with ferric chloride a deep blue coloration, which rapidly changes to dirty-yellow. C. F. B.

Synthesis of 2-Dimethylhydrindole. By C. Paal and E. Laudenheimer (*Ber.*, **25**, 2974—2978).—Attempts to obtain alkyl derivatives of orthamidobenzyl alcohol by treating it with alkyl iodides having failed, the authors endeavoured to obtain these derivatives by the reduction of the condensation products of the alcohol with aldehydes and ketones (see this vol., p. 23). Isopropyleneorthamidobenzyl

alcohol is readily reduced by sodium in alcoholic solution, with formation of *isopropylorthamidobenzyl alcohol*, $NHPr^{\beta}\cdot C_6H_4\cdot CH_2\cdot OH$, which forms a yellowish oil, sparingly soluble in water, but readily in mineral acids and organic solvents. It distils between 210° and 260°, undergoing partial decomposition; if it is boiled in connection with a reflux apparatus for two hours, the decomposition is complete, the products being water and a colourless oil, which has the composition $C_{10}H_{13}N$; it boils at 210° (uncorr.), is almost insoluble in water, but dissolves readily in mineral acids, and has a faint, turpentine-like odour. The elimination of water from isopropylorthamidobenzyl alcohol might take place in three different ways, with formation of the following compounds:—

$$C_6H_4<\begin{matrix}NPr^{\beta}\\ |\\ CH_2\end{matrix}; \quad C_6H_4<\begin{matrix}NH_2\\ |\\ CH_2\end{matrix}>CMe_2; \quad C_6H_4<\begin{matrix}NH\cdot CHMe\\ |\\ CH_2\cdot CH_2\end{matrix}.$$

The first formula cannot, however, represent the constitution of the compound, as it yields a nitroso-derivative, and must, therefore, be a secondary base; the substance represented by the third formula is tetrahydroquinaldine, which has already been prepared (Abstr., 1881, 742; 1884, 183), and has properties quite different from those of the authors' compound. There remains, therefore, only the second formula, according to which the substance is 2-*dimethylhydrindole*, and with this supposition its properties fully agree.

2-Dimethylhydrindole combines with ethyl iodide to form the *ethiodide*, which separates from ether in well developed prisms. The *nitrosamine*, $C_{10}H_{12}N\cdot NO$, is a reddish-brown oil, which decomposes on distillation, even in a vacuum; the *hydrochloride*, $C_{10}H_{13}N,HCl$, crystallises from water in slender, white needles, and melts at 150° with decomposition; the *platinochloride*, $(C_{10}H_{13}N)_2,H_2PtCl_6$, crystallises in orange-red plates, melts at 200° with decomposition, and is readily soluble in water. H. G. C.

Bidiphenylenethylene: A Red Hydrocarbon. By C. Graebe (*Ber.*, **25**, 3146—3149).—By passing fluorene over heated lead oxide, de la Harpe and van Dorp (this Journal, 1876, i, 242) obtained a red hydrocarbon $C_{26}H_{16}$. Mantz (*Inaug. Diss.*, *Geneva*, 1892) found that the same compound was formed by heating fluorene with bromine at 240—300°, or by passing a current of chlorine into fluorene at a temperature of 280—290°; also by heating fluorene with sulphur. He established its molecular weight, and assigned to it the constitution $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C:C<\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$, inasmuch as it combined with two equivalents of halogen, yielded diphenylene ketone on oxidation, fluorene on heating it with zinc dust, and a colourless hydrocarbon $C_{26}H_{18}$ on hydrogenation. The author finds that bidiphenylenethylene is best prepared by heating a mixture of lead oxide and fluorene to the boiling point of the latter, and finally for a short time at 350°, extracting the product with carbon bisulphide, and crystallising the residue from alcohol and chloroform or carbon tetrachloride, when the pure hydrocarbon is obtained in yellowish-red needles and prisms, the colour being intermedi-

ate between those of potassium dichromate and chromic anhydride. It melts at 187—188° (corr.), and cannot be decolorised; indeed further purification tended to increase the brightness of its colour. It forms a colourless dibromide, $C_{26}H_{16}Br_2$, a solution of which in toluene becomes red on warming it with sodium, due to the reproduction of the hydrocarbon. The colour of bidiphenylenethylene is apparently to be ascribed to the presence of the group $=C{\cdot}C=$, as both the dibromide and the hydrocarbon $C_{26}H_{18}$ (bidiphenylenethane) are colourless. The atomic grouping of the red hydrocarbon is thus analogous to that of azobenzene, but the doubly-linked carbon atoms exert less influence on the colour than do the doubly-linked nitrogen atoms, inasmuch as diphenylethylene and tetraphenylethylene are both colourless (compare, however, Armstrong, Proc., 1892, 192). Its further study is being continued. A. R. L.

Derivatives of 1 : 4-Amidonaphthalene. By R. Henriques (*Ber.*, **25**, 3058—3068).—1 : 4-Nitroethoxynaphthalene (Hermann, Abstr., 1891, 1379; Grandmougin and Michel, Abstr., 1892, 862) is conveniently prepared by dropping α-ethoxynaphthalene into nitric acid of 28° Baumé (1½ parts) at 60°, the yield being 90 per cent. of the ethoxynaphthalene employed. In addition to the description given of the corresponding amido-derivative (*loc. cit.*), it is to be mentioned that when ferric chloride is added to solutions of its salts, a copious indigo-blue precipitate separates, and on boiling, α-naphthaquinone is formed.

1 : 4-*Acetamidoethoxynaphthalene* is economically prepared by adding a mixture of amidoethoxynaphthalene hydrochloride (2 parts) and sodium acetate (3 parts), together with a trace of stannous chloride, to a cold solution of phosphoric chloride (1 part) in glacial acetic acid (4 parts), and boiling for a short time. It crystallises from alcohol or glacial acetic acid in long, colourless needles, melts at 189°, and is as good as insoluble in water, and somewhat sparingly soluble in boiling alcohol. 1 : 4-*Nitromethoxynaphthalene* melts at 83°, and the corresponding *acetamido*-compound melts at 187°. 1 : 4-Amidoethoxybenzene (phenetidine) is not attacked by nitric acid in the cold, but when boiled with it, the odour of quinone is perceptible; whereas the acetyl derivative (phenacetine), according to Autenrieth and Hinsberg (Abstr., 1892, 160), is converted by dilute nitric acid into the nitro-derivative [$OEt : NO_2 : NHAc = 4 : 2 : 1$], an observation which the author confirms.

When 1 : 4-acetamidoethoxynaphthalene is treated with cooled nitric acid of 26° Baumé, a *compound*, $C_{28}H_{34}N_2O_5$, is obtained, which crystallises from alcohol in yellow needles, melts at 218—219°, is insoluble in water and in alkalis, and decomposes with the evolution of acetic acid, if boiled with sulphuric acid. The same compound is obtained together with α-naphthaquinone when 1 : 4-acetamidoethoxynaphthalene is boiled with dilute nitric acid.

When 1 : 4-amidoethoxynaphthalene hydrochloride is treated with nitric acid of 20° Baumé (10 parts), α-naphthaquinone separates, whilst on adding ferric chloride and hydrochloric acid to the filtrate, a yellow crystalline precipitate falls, which is sparingly soluble in

alcohol, readily so in water, but reprecipitated on the addition of hydrochloric acid; it is a *double salt* of the diazo-derivative, and similar compounds are obtained on adding chromic acid or mercuric chloride and hydrochloric acid to a solution of diazotised amidoethoxynaphthalene.

When 1 : 4-amidoethoxybenzene (10 grams) is dissolved in a mixture of alcohol (50 grams) and 50 per cent. acetic acid (25 grams), and a 10 per cent. solution of sodium nitrite (26 c.c. = 0·5 mol.) added, the *diazoamido*-derivative, $C_{16}H_{19}N_3O_2$, separates in yellow needles; water is now added, and as soon as the precipitation is complete, the compound is collected and washed successively with water and alcohol. It cannot be recrystallised, as it undergoes decomposition; it melts at 89—91°, and combines with phenols to form hydroxyazo-compounds. The author has not as yet succeeded in converting it into the amidoazo-derivative, but it yields a crystalline compound when treated with alcohol, which will be described in a future paper.

When 1 : 4-amidoethoxynaphthalene is treated with nitrous acid, in the manner just described, it yields *amidoazoethoxynaphthalene*, $C_{24}H_{23}N_3O_2$, which crystallises from benzene in red needles, melts at 175°, and is readily soluble in benzene, sparingly so in alcohol and glacial acetic acid, and insoluble in water. It is a feeble base, yielding yellow salts which dissolve sparingly in alcohol, forming green solutions, dissociate in the air, and are decomposed when boiled with water. On reduction with stannous chloride and hydrochloric acid, a mixture of compounds, which are being further investigated, is obtained; one of the most soluble salts from this mixture yields, on acetylation, a compound $OEt{\cdot}C_{10}H_5(NHAc)_2$, melting at 254°.

A. R. L.

Action of Phenylhydrazine on Cantharidin. By L. Spiegel (*Ber.*, **25**, 2956—2960).—The substance obtained in small quantities together with cantharidinphenylhydrazone by the action of phenylhydrazine on cantharidin (Abstr., 1892, 999) may be obtained pure by frequent recrystallisation from acetone and subsequently from absolute alcohol, and drying at a temperature not exceeding 105°. It has then the composition $C_{16}H_{20}N_2O_4$, and melts at 194°; the author proposes for it the name *cantharidinphenylhydrazone hydrate*. When it is heated with an excess of phenylhydrazine, with aniline, with alcoholic potash, or by itself above 105°, it loses the elements of water, forming cantharidinphenylhydrazone. The author believes that the compound is formed by the direct union of phenylhydrazine with the carbonyl group of cantharidin without simultaneous elimination of water, according to which its constitution would be represented by the formula $C_9H_{12}O_3{\cdot}C(OH){\cdot}NH{\cdot}NHPh$.

If cantharidin is allowed to remain with an excess of phenylhydrazine at the ordinary temperature, it yields a substance which, although it has not been obtained pure, appears to be the *phenylhydrazide of cantharic acid*, $COOH{\cdot}C_8H_{12}O{\cdot}CO{\cdot}NH{\cdot}NHPh$. All attempts to purify it by recrystallisation were unsuccessful, owing to the ease with which it passes into cantharidinphenylhydrazone.

H. G. C.

Chlorophyll. Part IV. By E. Schunck (*Proc. Roy. Soc.*, **50**, 302—317; compare Abstr., 1887, 972; 1889, 279).—When the residue obtained by evaporating to dryness a solution of phyllocyanin in aqueous potash is heated nearly to fusion, it suddenly turns brown. The aqueous solution of the mass, on treatment with acetic acid, gives a bulky, brown precipitate, which is ultimately obtained in lustrous, plum-coloured needles. It is soluble in concentrated hydrochloric acid, glacial acetic acid, chloroform, ether, or boiling alcohol, and insoluble in carbon bisulphide. The solutions are crimson, and their spectra show no absorption bands at the red end. This substance is possibly identical with Hoppe-Seyler's dichromatic acid or phylloporphyrin.

On treating chlorophyll with concentrated acids, phylloxanthin is formed in addition to phyllocyanin; concentrated hydrochloric acid extracts the latter from the ethereal solution of the two substances, and on exposing the ethereal solution to the air, brown cakes are obtained, which are dissolved in a little chloroform, alcohol added, the deposit washed with alcohol, dried, and dissolved in boiling glacial acetic acid. Phylloxanthin is deposited on cooling and is again dissolved in hot acetic acid, allowed to separate, and after being deposited several times from ether, is obtained as a dark green, amorphous powder still containing a little fatty matter. It sometimes separates from its ethereal solution in small, stellate groups, but is deposited from boiling alcohol in a granular state; it is soluble in ether, carbon bisulphide, benzene, aniline, light petroleum, and chloroform, giving brownish-green, fluorescent solutions. It begins to decompose at 160°, and on burning, leaves a residue of ferric oxide; iron seems to be an essential constituent. Nitric or chromic acid turns its acetic acid solution deep yellow; with concentrated nitric acid, phylloxanthin yields oxalic acid. The chloroform solution is bleached by light on exposure to air; bromine in small quantities turns the chloroform solution bright green, whilst excess of bromine gives a yellow colour. A dark blue solution is obtained with concentrated hydrochloric or sulphuric acid. The reactions with copper acetate, ferrous oxide, silver oxide, metallic tin in acid solution, and alcoholic alkalis are described.

"Alkaline chlorophyll" is best prepared by extracting fresh grass leaves with boiling alcohol (80 per cent.); the solution is filtered hot, and, on cooling, deposits crude chlorophyll. This is boiled for some time with alcoholic soda, filtered, and the filtrate saturated with carbonic anhydride. The precipitate is extracted with cold alcohol, saturated sodium chloride solution added to the solution, the precipitate dissolved in boiling alcohol, and the solution evaporated to dryness. The residue, after washing with a little cold water, is found to be a sodium compound; on treatment with the requisite quantity of acetic acid, extracting with ether, and evaporating the ethereal solution, a green substance free from sodium is obtained. This the author terms *alkachlorophyll*. It is amorphous, soluble in alcohol, ether, chloroform, benzene, carbon bisulphide, or aniline, giving bluish-green solutions exhibiting a red fluorescence; but insoluble in boiling water and light petroleum. Its solutions are

much more stable towards light than are those of chlorophyll. With acetic acid, it seems to yield phyllotaonin. W. J. P.

Trichosanthin and Thallochlore. By TSCHIRCH (*Chem. Centr.*, 1892, ii, 80; from *Schweiz. Woch. Pharm.*, **30**, 221—222).—If the succulent part of the fruit of *Trichosanthes pubera* is extracted with ether, a red pigment is removed, which was only examined spectroscopically. If the residue is now extracted with alcohol, a green pigment, *trichosanthin*, is dissolved out; it can be purified by dissolving it in hydrochloric acid and reprecipitating with water. It is a black powder, and its solution in hydrochloric acid is blue. It is the first green pigment obtained from plants which is not identical with chlorophyll, as thallochlore from the gonidia of *Cetraria islandica* is identical with the latter. C. F. B.

Affinity Coefficients of some Pyrroline and Indole Acids. By A. ANGELI (*Gazzetta*, **22**, ii, 1—31).—The author has measured the electrical conductivity of the acids given in the following table:—

	K.
α-Pyrrolinecarboxylic acid	0·00403
n-Methylpyrrolineglyoxylic acid	2·7
α-Acetyl-α-pyrrolinecarboxylic acid	0·0305
Metadimethyl-β-pyrrolinecarboxylic acid	0·000075
Paradimethyl-β-pyrrolinecarboxylic acid	0·00011
Metadimethylpyrrolinedicarboxylic acid	0·00213
α-Indolecarboxylic acid	0·0177
β-Indolecarboxylic acid	0·00056
β-Methyl-α-indolecarboxylic acid	0·0047
β-Methyl-β-indolecarboxylic acid	0·00013
Methylindoleacetic acid	0·00215
Benzoylpyruvic acid	0·65
Phenyloxazolic acid	0·55
Thiophenpyruvic acid	0·46
Pyrrolinepyruvic anhydride	0·089
Bromocitraconic anhydride	1·49
Dibromacetylacrylic acid	0·0061
Apiolic acid	0·00803
Apionylketonic acid	3·35
Acetonedicarboxylic acid	0·079

In solutions of pyrrolineglyoxylic acid the value of 100 *k* diminishes enormously with increased dilution; this is probably due to the great readiness with which the aqueous solution changes on exposure to the air. The constant *K* is certainly greater than 0·967.

The affinity coefficients of dibromomethylpyrrolineglyoxylic acid and paradimethylpyrrolinedicarboxylic acid are so great that the author was unable to determine them.

The aqueous solution of metadimethyl-α-pyrrolinecarboxylic acid changes so rapidly that concordant results could not be obtained with it.

From the data afforded by the indole- and methylindole-carboxylic acids, the author shows that β-pyrrolinecarboxylic acid should have an

affinity coefficient $K = 0{\cdot}00012$. It is noteworthy that in all the cases examined, the presence of a methyl group in proximity to the carboxyl group greatly diminishes the affinity coefficient. The very high coefficient found for dibromacetylacrylic acid renders it probable that the substance has the constitution $CBr\lessgtr^{CBr}_{COO}\gtrOMe{\cdot}OH$.

W. J. P.

Action of Piperidine and Pyridine on Haloïd Salts of Cadmium. By R. Varet (*Compt. rend.*, **115**, 464—466).—Dry and finely powdered cadmium chloride slowly combines with piperidine at 25° and yields a bulky, white, amorphous compound, $CdCl_2,2C_5H_{11}N$, very slightly soluble in piperidine, decomposed by water, and unstable when exposed to air. Cadmium bromide under similar conditions yields small, hard, brilliant, white crystals of the compound $CdBr_2,2C_5H_{11}N$, which is decomposed by water. If warm piperidine is saturated with cadmium bromide, the compound $CdBr_2,3C_5H_{11}N$ separates in small crystals on cooling; it alters when exposed to air, and is only slightly soluble in piperidine. Cadmium iodide yields two analogous crystalline compounds.

Pyridine with cadmium chloride yields only the compound $CdCl_2,2C_5H_5N$; cadmium bromide yields the compound $CdBr_2,6C_5H_5N$; cadmium iodide, the compound $CdI_2,6C_5H_5N$. C. H. B.

Action of Bromine on Aldehydecollidine. By P. Knudsen (*Ber.*, **25**, 2985—2989).—*Bromethyl-α-picoline*, $C_5NH_3Me{\cdot}CHMeBr$, is obtained by heating aldehydecollidine (10 grams) dissolved in the calculated quantity of concentrated hydrochloric acid with bromine (26·5 grams) for 10—12 hours at 100°. The product is dissolved in ether, treated with sulphurous acid, and excess of soda added. The ethereal solution is then separated, shaken with dilute acetic acid, then with dilute alkali, and dried over calcium chloride. On distilling the ether in a vacuum, a thick, bright-yellow oil is obtained which has an aromatic, disagreeable, penetrating odour, and is too unstable to be analysed. The *picrate* crystallises from benzene in compact prisms or needles, and melts at 154°.

α-Picolyl-β₁-methylalkine, $C_5NH_3Me{\cdot}CHMe{\cdot}OH$, is obtained as *picrate* on boiling the above bromocollidine picrate with a large quantity of water. It crystallises in broad leaflets or tablets, and melts at 164°. The *free base* is obtained by cautiously treating the picrate with a solution of sodium hydroxide and then extracting with ether. It boils at 240° with slight decomposition, is a colourless, viscid oil, soluble in water, and solidifies to a crystalline mass which melts at blood-heat. When oxidised in the cold with dilute permanganate, it yields methylnicotinic acid (m. p. 209—210°).

50 grams of aldehydecollidine yield 110 grams of crude bromocollidine picrate and 31 grams of crude, or 14 grams of the pure alkine boiling at 240°.

α-Picolyl methyl ketone, $C_5NH_3Me{\cdot}COMe$, is obtained by oxidising the above alkine dissolved in acetic acid with the calculated quantity of chromic acid dissolved in acetic acid (50 per cent.) at 60—70°. It boils at 230—240°, is a colourless limpid liquid, quickly turns brown,

and is easily soluble in water. The *oxime*, which is sparingly soluble in water, crystallises from dilute alcohol in beautiful needles, and melts at 182°. E. C. R.

Oxidation of Quinoline by Potassium Permanganate. By A. Golenkin and A. Klepikoff (*J. Russ. Chem. Soc.*, **22**, 535—548).—Quinoline prepared synthetically by Skraup's reaction, when oxidised by permanganate solution, whether hot (60°) or cold, gives nothing but quinolinic and oxalic acids, no other crystalline acid being formed. The yield of quinolinic acid varies, according to the proportions of quinoline and permanganate taken, from 11 to 28 per cent. of the quinoline employed, the greatest yield being obtained with 6·66 mols. of permanganate to 1 mol. of quinoline, and a 3·7 per cent. solution of the oxidant. Cooling does not increase the yield. When coal-tar quinoline is oxidised in the same way, other crystalline acids, besides oxalic and quinolinic, are formed; one of these melts at 168°. J. W.

New Synthesis of Pyrazole Derivatives. By A. Bischler (*Ber.*, **25**, 3143—3145).—The formation of hydrazones from ethyl acetoacetate or its alkyl derivatives, and diazobenzene salts, has been observed by Japp and Klingemann, and by V. Meyer. If a concentrated aqueous solution of diazobenzene chloride (1 mol.) is slowly poured, with cooling, into mixed alcoholic solutions containing equivalent proportions of ethyl acetophenoneacetoacetate (Paal, Abstr., 1884, 598) and sodium, and after remaining for half an hour, an excess of water is added to the mixture, an oil separates which at the end of 24 hours is washed with water, redissolved in alcohol, and digested with sodium hydroxide, whereby Beyer and Claisen's diphenylpyrazolecarboxylic acid (Abstr., 1887, 944) is isolated. When the acid is heated above its melting point, 1 : 5-diphenylpyrazole (*loc. cit.*) is formed; the latter is readily soluble in alcohol, ether, and benzene, but insoluble in water, and yields a crystalline platinochloride. A. R. L.

Oxazine Dyes. By R. Nietzki and A. Bossi (*Ber.*, **25**, 2994—3005).—The authors propose to modify the nomenclature of these compounds as given by Möhlau (Abstr., 1892, 887). They propose to substitute the name *oxazone* for quinoxazone and *oxazime* for quinoxazine. For the corresponding compounds of the methylene-blue series, they propose the names *thiazone* and *thiazime;* and they designate derivatives in which the imido-group is replaced by the ammonium group by changing the ending "azime" into "azimium."

Nietzki and Otto (*Ber.*, **21**, 1745) have stated that 2 mols. of aniline combine with gallocyanin with elimination of 1 mol. H_2O. On repeating the experiment, the authors find that only 1 mol. of aniline combines with elimination of 1 mol. of carbonic anhydride and 1 mol. of hydrogen and a compound of the formula $C_{20}H_{17}N_3O_3$ is obtained. By conducting the experiment in a suitable apparatus, an absorption of atmospheric oxygen is observed; but the yield (50—60 per cent.) is the same whether the experiment is performed in air or in an atmosphere of carbonic anhydride.

The methyl ether of gallocyanin, "prune," combines in molecular proportion with aniline, giving a compound of the formula

$$C_{22}H_{21}N_3O_5,$$

and in this reaction no absorption of oxygen is observed.

If gallocyanin and aniline are rubbed together in the cold, a crystalline compound is formed without evolution of carbonic anhydride; this compound is not a simple aniline salt of gallocyanin, for when treated with dilute hydrochloric acid gallocyanin is not regenerated. The compound cannot be purified by crystallisation, and when gently heated is converted into gallocyaninanilide. The authors represent gallocyaninanilide by the formula $NMe_2{\cdot}C_6H_3{<}\overset{O}{\underset{N}{>}}C_6HO(OH){\cdot}NHPh$ [OH : O : NHPh = 1 : 2 : 4].

Meldola's naphthol-blue combines with 1 mol. of aniline with evolution of 1 mol. of hydrogen. The commercial zinc double salt of Meldola's blue is converted into nitrate by means of dilute nitric acid, and the nitrate warmed with excess of aniline on the water-bath. This nitrate is converted first into the base, and then into hydrochloride.

The *hydrochloride* is somewhat sparingly soluble in water and cold alcohol, crystallises from hot alcohol in long needles having a green lustre, and must be crystallised in the presence of hydrochloric acid, as it tends to decompose in solution. The *free base* is obtained in slender, shining, brown needles by adding ammonia to a hot alcoholic solution of the hydrochloride; it melts at 275° and is insoluble in water and hot alcohol. The salts impart to animal fibres and cotton mordanted with tannin a greenish-blue shade, which is changed to red by dilute alkalis. The base most probably has the constitution $NMe_2{\cdot}C_6H_3{<}\overset{O}{\underset{N}{>}}C_{10}H_5{:}NPh$, and is therefore a phenylated Nile-blue, and should be obtained by the action of nitroso-dimethylmetamidophenol on phenyl-α-naphthylamine. The authors have prepared the compound by the latter method, and find that the two preparations are identical, giving the same melting point and the same absorption spectra.

From the above results, the authors conclude that Witt's cyanamine obtained by the action of dimethylparaphenylenediamine on Meldola's blue is a dimethylamido-derivative of the above compound, and has the formula $NMe_2Cl{:}C_6H_3{<}\overset{O}{\underset{N}{>}}C_{10}H_5{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$.

Muscarine behaves in a very similar manner to Meldola's blue. The *hydrochloride* is sparingly soluble in cold water, more easily in hot water, crystallises in slender, violet needles, and has the composition $NMe_2Cl{:}C_6H_3{<}\overset{N}{\underset{O}{>}}C_{10}H_5{\cdot}OH(\beta)$. The free base is obtained by adding ammonia to a solution of the salt, and forms a precipitate having a violet lustre; it is soluble in potassium or sodium hydroxide.

Aniline combines with the salts of muscarine with even greater readiness than with those of Meldola's blue. The *hydrochloride* of

the compound thus produced has the composition $C_{24}H_{20}N_3O_3Cl$, crystallises in green needles, and dissolves in alcohol with a greenish-blue coloration. The *free* base is obtained in needles having a brown lustre and gives red solutions. E. C. R.

Indazole Derivatives. By O. N. Witt, E. Noelting, and E. Grandmougin (*Ber.*, **25**, 3149—3156; compare Abstr., 1891, 312).—Acetylnitroindazole (*loc. cit.*) crystallises from alcohol in long, flat needles, melts at 140°, and yields amidoindazole (m. p. 210°) on treatment with alcoholic ammonium sulphide.

Acetamidoindazole, $NHAc{\cdot}C_6H_3<\begin{matrix}CH\\|\\N-\end{matrix}>NH$, formed by boiling the last-mentioned amidoindazole with glacial acetic acid for 12 hours, crystallises from alcohol in long, white needles, melts at 248°, sublimes undecomposed, but undergoes oxidation in solution. It dissolves in concentrated hydrochloric acid, and the solution diluted with water is only diazotised on boiling it with nitrite; the compound may be readily diazotised after heating it with sodium hydroxide solution.

Acetamidoacetylindazole, $NHAc{\cdot}C_6H_3<\begin{matrix}CH\\|\\N-\end{matrix}>NAc$, is obtained, together with the last described derivative, when the amidoindazole is boiled with acetic anhydride for some time, and being less soluble in water than acetamidoindazole, separates from the solvent in slender, felted needles, melts at 184—185°, and distils undecomposed. It is soluble in an excess of concentrated hydrochloric acid, is not precipitated on adding water, and cannot be diazotised until it is hydrolysed.

In the preparation of hydroxyindazole (*loc. cit.*), it is advisable to employ a fairly concentrated solution, and after boiling the diazo-solution, to neutralise it before extracting with ether. It crystallises from boiling water in lustrous leaflets, melts at 215—216°, and its alkaline solution, on the addition of diazosulphanilic acid, gives an orange-red colouring matter. No trace of an indazole derivative is formed by heating the diazo-derivatives of nitrometaxylidine [$Me_2 : NO_2 : NH_2 = 1 : 3 : 4 : 6$] or nitrorthotoluidine [$Me : NO_2 : NH_2 = 1 : 4 : 6$].

The *diazoamido*-derivative of nitrotoluidine [$Me : NH_2 : NO_2 = 1 : 2 : 4$] is prepared by dissolving the nitrotoluidine (31 grams) in glacial acetic acid (400 c.c.) and adding by degrees an aqueous solution of sodium nitrite (7 grams) to the cooled solution. It is insoluble in water, and only sparingly soluble in most solvents. It is best purified by very cautiously crystallising it from hot glacial acetic acid, from which it separates in yellow needles; it melts at 200—201° with the evolution of gas. When boiled for a long time with glacial acetic acid (5 parts), nitroindazole (m. p. 177—178°) is formed; (compare Heusler, Abstr., 1892, 456). A. R. L.

2′-Paratolylindazole. By C. Paal and E. Fritzweiler (*Ber.*, **25**, 3167—3172; compare Abstr., 1891, 723; 1892, 67).—*2′-Paratolyl-*

indazole, $C_6H_4<\begin{matrix}CH\\|\\N\end{matrix}>N\cdot C_6H_4Me$, is obtained by boiling equal weights of orthonitrobenzylparatoluidine (Lellmann and Stickel, Abstr., 1886, 793), dissolved in alcohol, with tin and hydrochloric acid until dissolution is complete, gently warming the *stannochloride* which separates on cooling with an excess of ammonium polysulphide, and diluting with water, when a mixture of the base and tin sulphide is precipitated. On extracting this with boiling absolute alcohol, the indazole separates from the filtrate in long, white, lance-shaped crystals; it melts at 105°, distils undecomposed, and is insoluble in water. It has only feeble basic properties; the *hydrochloride* crystallises from concentrated hydrochloric acid in white needles, and is dissociated by water.

Paratolueneorthazobenzoic acid, $C_6H_4Me\cdot N_2\cdot C_6H_4\cdot COOH$, is formed when the indazole, dissolved in glacial acetic acid, is treated with rather more than 2 mol. proportions of chromic anhydride in the same solvent. On adding water, it separates as an oil which subsequently solidifies; this is dissolved in dilute ammonia and reprecipitated by hydrochloric acid. The pure compound crystallises from dilute alcohol in red needles, and melts at 115°. The *alkali* salts are soluble in water, and their solutions give no precipitates with calcium, barium, or magnesium salts, but a red, flocculent precipitate with aluminium chloride, and an orange precipitate with silver nitrate.

Paratoluenehydrazobenzoic acid, $C_6H_4Me\cdot NH\cdot NH\cdot C_6H_4\cdot COOH$, is produced by gently warming a dilute ammoniacal or alcoholic solution of the azo-acid with zinc dust. It crystallises from dilute alcohol in yellowish leaflets, melts at 144°, and its solutions oxidise in the air. The *alkali* salts are soluble in water, and their solutions give with barium chloride a white precipitate soluble on boiling; silver nitrate gives a white precipitate which immediately becomes black. An *acid* isomeric with that just described is obtained when a dilute alcoholic solution of paratolueneorthoazobenzoic acid is boiled with tin and hydrochloric acid. It crystallises from ethyl acetate in bunches of white needles, and melts at 198°. The *alkali* salts are soluble in water, and the *silver* salt is a white precipitate which only gives a metallic mirror on heating. The constitution of the acid is being determined. A. R. L.

Phenometadiazine Derivatives. By A. Bischler and D. Barad (*Ber.*, **25**, 3080—3097; compare Bischler, Abstr., 1891, 745).—Acetylorthamidobenzophenone melts at 88·5—89°, not at 72° as stated by Auwers and Meyenburg (Abstr., 1891, 1375); it is readily soluble in ether, hot alcohol, and hot benzene, but insoluble in cold water.

Pheno-2'-methyl-4'-phenylmetadiazine, $C_6H_4<\begin{matrix}CPh:N\\|\\N=CMe\end{matrix}$, is obtained when acetylorthamidobenzophenone is heated at 170° for three hours with concentrated alcoholic ammonia; it is a yellowish, crystalline compound, melts at 47—48°, boils at 349—353°, and is readily soluble

in alcohol, ether, and benzene, but almost insoluble in water. A vapour density determination, carried out under reduced pressure, gave results which showed that its molecular formula is $C_{15}H_{12}N_2$. It is not decomposed by concentrated hydrochloric acid even at 200—210°. The *hydrochloride*, $C_{15}H_{12}N_2,HCl$, prepared by passing hydrogen chloride into an ethereal solution of the base, separates from alcoholic ether in colourless crystals, and is very readily soluble in water and alcohol, but insoluble in ether. The *platinochloride*, $(C_{15}H_{12}N_2)_2,H_2PtCl_6$, crystallises from hot alcohol in flat, orange needles, decomposes at 160°, and is readily soluble in hot alcohol, but almost insoluble in cold water. The *picrate*, $C_{15}H_{12}N_2,C_6H_3N_3O_7$, crystallises from hot dilute alcohol in dark yellow needles, decomposes at 170°, and is only sparingly soluble in boiling water. The *mercurochloride*, $C_{15}H_{12}N_2,HHgCl_3 + H_2O$, separates from hot water in lustrous, greyish needles, and loses its water at 100—115°. The *methiodide*, $C_{15}H_{13}N_2,MeI$, is formed when the base is heated with methyl iodide at 120°; it separates from hot alcohol in the form of a heavy powder, melts at 190°, and is rather sparingly soluble in cold water, alcohol, and ether. The *ethiodide*, $C_{15}H_{12}N_2,EtI$, forms lemon-yellow needles, melts at 204°, and is rather more readily soluble in warm alcohol and water than the methiodide.

Propionylorthamidobenzophenone, $COEt\cdot NH\cdot C_6H_4\cdot COPh$, prepared by warming the amidoketone with propionic anhydride, crystallises from dilute alcohol in lustrous, colourless needles, melts at 78·5°, and is readily soluble in hot alcohol, benzene, and ether.

Pheno-2′-ethyl-4′-phenylmetadiazine, $C_{16}H_{14}N_2$, prepared by heating the preceding compound at 170° with alcoholic ammonia, crystallises from hot dilute alcohol in flat, colourless needles, melts at 83°, and is soluble in 12·01 parts of 94 per cent. alcohol at 19°, and in 11·18 parts of benzene at the same temperature; molecular weight determinations by the freezing point and by the vapour density methods gave results agreeing with those required by a compound of the above molecular formula. The *platinochloride*, $(C_{16}H_{14}N_2)_2,H_2PtCl_6$, crystallises from hot dilute alcohol in small, yellow plates, decomposes at about 200—205°, and is insoluble in ether, but readily soluble in boiling alcohol and water. The *picrate*, $C_{16}H_{14}N_2,C_6H_3N_3O_7$, crystallises from hot alcohol in long, yellow needles, and decomposes at 150°; it dissolves freely in hot water and alcohol.

Butyrylorthamidoacetophenone, $COPr\cdot NH\cdot C_6H_4\cdot COPh$, separates from alcohol in well-defined, colourless, rhombic crystals, melts at 56°, and dissolves freely in hot ether, alcohol, and benzene, but only sparingly in the cold solvents.

Pheno-2′-propyl-4′-phenylmetadiazine, $C_{17}H_{16}N_2$, crystallises from hot dilute alcohol in yellowish needles, melts at 99—100°, and is soluble in 11·37 parts of 94 per cent. alcohol and in 11·58 parts of benzene at 19°. The *platinochloride*, $(C_{17}H_{16}N_2)_2,H_2PtCl_6$, is a reddish-yellow, crystalline compound, melts at 203°, and is only sparingly soluble in water and alcohol. The *picrate*, $C_{17}H_{16}N_2,C_6H_3N_3O_7$, crystallises in microscopic, light yellow needles, sinters at 140°, melts at 150° with decomposition, and is readily soluble in hot water and alcohol. The *mercurochloride*, $C_{17}H_{16}N_2,HHgCl_3 + H_2O$, separates from boiling

water, in which it is only sparingly soluble, in lustrous, colourless needles, and loses its water at 100°.

Pheno-2'-isopropyl-4'-phenylmetadizine, $C_{17}H_{16}N_2$, is formed when the oily product of the action of orthamidobenzophenone on isobutyric anhydride is heated with alcoholic ammonia at 170°; it crystallises from alcohol in well-defined needles, and melts at 99°. The *platinochloride*, $C_{17}H_{16}N_2,H_2PtCl_6$, is a vermilion-coloured powder, melting at 160° with previous decomposition. The *picrate*, $C_{17}H_{16}N_2,C_6H_3N_3O_7$, crystallises from alcohol in yellow needles, melts at 140° with decomposition, and is only sparingly soluble in cold water or alcohol.

Benzoylorthamidoacetophenone, $NHBz{\cdot}C_6H_4{\cdot}COPh$, crystallises from dilute alcohol in colourless needles, and melts at 80·5°; it is readily soluble in warm benzene and alcohol, but only sparingly in ether or cold alcohol.

Pheno-2'-4'-diphenylmetadiazine, $C_{20}H_{14}N_2$, prepared by heating the preceding compound with alcoholic ammonia, crystallises from alcohol in long, colourless needles, sinters at 119°, and melts at 120°; it is soluble in 21·85 parts of 94 per cent. alcohol and in 15·64 parts of benzene at 17°, and dissolves freely in hot concentrated hydrochloric acid. The *platinochloride*, $(C_{20}H_{14}N_2)_2,H_2PtCl_6$, is a reddish, crystalline powder only sparingly soluble in hot alcohol; it melts at 180°. The *picrate*, $C_{20}H_{14}N_2,C_6H_3N_3O_7$, is a yellow powder.

Pheno-4'-phenylmetadiazine-2'-carboxylic acid is obtained in small quantities when phenoethylphenylmetadiazine is oxidised with chromic acid in sulphuric acid solution; it is a yellow, crystalline compound, and readily undergoes decomposition with liberation of carbonic anhydride and formation of pheno-4'-phenylmetadiazine. The *silver* salt, $C_{14}H_9N_2{\cdot}COOAg$, is a voluminous, amorphous compound.

Pheno-4'-phenylmetadiazine picrate, $C_{14}H_{10}N_2,C_6H_3N_3O_7$, crystallises from hot dilute alcohol in small, yellow plates, melts at 178°, and is only sparingly soluble in cold water and alcohol, but readily in the hot solvents.

Tetrahydropheno-2'-methyl-4'-phenylmetadiazine is formed when phenomethylphenylmetadiazine is reduced with sodium and boiling amyl alcohol; it is a brown oil, dissolves freely in the ordinary organic solvents, and gives badly characterised salts with the usual reagents. The *dibenzoyl* derivative, $C_{29}H_{24}N_2O_2$, prepared by heating the base with benzoic anhydride on the water-bath, separates from alcohol in almost colourless needles, melts at 188—189°, and is only sparingly soluble in cold alcohol, but readily in hot alcohol, ether, and benzene. When heated with concentrated hydrochloric acid at 140—150°, it is decomposed into benzoic acid and tetrahydrophenomethylphenylmetadiazine; the *picrate* of the regenerated hydro-base was obtained in yellow plates melting at 197°. F. S. K.

Quinazolines. By C. Wolff (*Ber.*, **25**, 3030—3040).—An extension of Gabriel and Jansen's work (Abstr., 1890, 1442; 1892, 217). Orthonitrobenzylphthalimide is prepared by heating a finely pulverised, intimate mixture of orthonitrobenzyl chloride (40 grams), potassium phthalimide (50 grams), and sodium chloride (135 grams), contained in a dry flask at 140° for about half an hour, and finally

raising the temperature to 170°. The product is extracted with boiling water, and the residue washed with 96 per cent. alcohol, when an amount of the phthalimide remains corresponding with 85 per cent. of the orthonitrobenzyl chloride employed. Orthonitrobenzylamine hydrochloride is obtained by heating equal weights of orthonitrobenzylphthalimide, hydrochloric acid (sp. gr. 1·19), and glacial acetic acid in a sealed tube at 170—190° for three hours; the crude product is washed with water to remove phthalic acid, and finally crystallised from 96 per cent. alcohol.

Gabriel and Jansen (*loc. cit.*) have noted the formation of phenylquinazoline and other compounds by the distillation of orthamidobenzylbenzamide. The author finds that when the last-named base is carefully heated at 250° until water ceases to be evolved, *dihydro-2'-phenylquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ N=CPh\end{matrix}$, is obtained; it crystallises from benzene in flat tables, and is soluble in the ordinary solvents. The *picrate* forms bright yellow needles, and melts at 161—162°; whilst the *platinochloride* is sparingly soluble in water, and melts at 210°. *Tetrahydro-2'-phenylquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ NH\cdot CHPh\end{matrix}$, is formed when the dihydro-compound (2·5 grams) is dissolved in alcohol (90 c.c.), and sodium (9 grams) gradually added; after crystallisation from light petroleum, it melts at 99—101°, is soluble in all ordinary solvents except water, and is readily decomposed by acids into benzaldehyde and orthobenzylenediamine, so that salts could not be prepared.

Orthonitrobenzylorthotoluylamide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4Me$, is prepared by shaking together in a closed flask an aqueous solution of orthonitrobenzylamine hydrochloride (1 mol.), a solution of sodium hydroxide (2 mols.), and orthotoluic chloride (1 mol.), collecting the product, and crystallising it from alcohol; it forms brilliant, colourless needles, and melts at 134—135°. *Orthamidobenzylorthotoluylamide* is obtained when a solution of the nitro-compound (40 grams) in 96 per cent. alcohol (10 parts) is mixed with an equal volume of hydrochloric acid (sp. gr. 1·13) and some zinc scraps, and the mixture kept cool for several hours. On shaking the clear solution with potash, the base separates as an oil, which is taken up with ether, whence it is isolated in a solid form; it crystallises from benzene in almost colourless needles, and melts at 114—116°. The *hydrochloride* melts at 211—214°, and the platinochloride at 208°. Under no conditions, either by heating the base or by the action of dehydrating agents, could it be converted into a quinazoline derivative.

Orthonitrobenzylparatoluylamide, prepared in the same way as the orthotoluyl derivative, melts at 140—142°, and remains unaltered when treated with zinc and hydrochloric acid, tin and hydrochloric acid, ammonium sulphide at 150°, or boiling hydriodic acid.

Orthonitrobenzylpropionamide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot COEt$, is prepared by boiling orthonitrobenzylamine hydrochloride (12 grams) with anhydrous sodium propionate (8 grams) and propionic acid (36 c.c.) for half an hour, neutralising the diluted solution with sodium

carbonate, dissolving the precipitated oil in ethyl acetate, and fractionally precipitating the compound with light petroleum; it crystallises in plates, melts at 61—62°, and is almost insoluble in water. *Orthamidobenzylpropionamide* is formed when tin and hydrochloric acid are added to an alcoholic solution of the nitro-compound, and the mixture kept cool for some hours; it melts at 68—70°, and the *platinochloride* melts at 184°. *Dihydro-2′-ethylquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ |\\ N=CEt\end{matrix}$, is obtained when the last-mentioned base is heated until water ceases to be evolved, and then distilled. It passes over at 290—300°, and, when crystallised from benzene, melts at 99—102°; the *tetrahydro*-derivative, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ |\\ NH\cdot CHEt\end{matrix}$, formed by reducing it in the manner described above under tetrahydrophenylquinazoline, melts at 86—88°.

Orthonitrobenzylethylamine, $NO_2\cdot C_6H_4\cdot CH_2\cdot NHEt$, is produced when a solution of orthonitrobenzyl chloride (15 grams) in absolute alcohol (150 c.c.) is heated on the water-bath for three hours in a closed vessel with 33 per cent. ethylamine solution (45 c.c.); the *hydrochloride* melts at 184—186°. *Orthonitrobenzylethylformamide*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NEt\cdot COH,$$

is obtained by boiling a mixture of the last-named base and dry sodium formate with absolute formic acid for four hours; after crystallisation from water, it melts at 65—67°. *Dihydro-3′-ethylquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NEt\\ |\\ N=CH\end{matrix}$, is formed when the formyl derivative is reduced with zinc and hydrochloric acid; the *picrate* melts at 170—172°, and the *platinochloride* at 199—202°. A. R. L.

Action of Alcoholic Potash on the Anilides, Toluidides, and Naphthalides of α-Bromopropionic, α-Bromobutyric, and α-Bromisobutyric Acids. By A. Tigerstedt (*Ber.*, **25**, 2919—2931).—The brominated acid anilides, &c., used were prepared by the action of a chloroform or toluene solution of the base on a similar solution of the brominated acid bromide.

Derivatives of α-Bromopropionyl, $NXH\cdot CO\cdot CHBr\cdot CH_3$.—The *anilide* forms colourless prisms, melting at 99°, sparingly soluble in light petroleum, easily so in chloroform, ether, alcohol, and benzene (see also Abstr., 1892, 1337). The *orthotoluidide*, $CHMeBr\cdot CO\cdot NH\cdot C_6H_4Me$, forms matted needles, insoluble in light petroleum, soluble in alcohol, benzene, ether, and chloroform, and melting at 131°. By the action of alcoholic potash, it yields two isomeric *diorthotolyl-αγ-diketo-βδ-dimethylpiperazines*, $C_6H_4Me\cdot N<\begin{matrix}CHMe\cdot CO\\ CO\cdot CHMe\end{matrix}>N\cdot C_6H_4Me$. Of these, the *para-modification* melts at 183—184°, and yields glistening scales, sparingly soluble in ether; the *anti*-modification forms small, agglomerated crystals melting at 155—162°, and more readily soluble in most solvents than the para-modification. The *paratoluidide* forms glistening scales, easily soluble in alcohol and chloroform, less so in benzene

and ether, insoluble in light petroleum. With alcoholic potash, it yields the two corresponding piperazines obtained by Goldblatt from paratoluidopropionic acid (Abstr., 1892, 1337). The *α-naphthalide* is soluble in alcohol, sparingly so in chloroform, benzene, and ether, crystallises in needles, and melts at 158°. With potash, it yields *α-dinaphthyl-αγ-diketo-βδ-dimethylpiperazine*, which was obtained in only one modification crystallising in plates melting at 220—224°. From the mother liquors from this piperazine, a substance was isolated which crystallised in rhombic plates melting at 140° with the evolution of a gas. On further heating, the liquid solidified again between 150° and 160°, and eventually fused with decomposition at 207—209°. The substance of melting point 207—209° had the composition $C_{11}H_{11}NO_2$. The *β-naphthalide* forms micaceous needles melting at 174°, sparingly soluble in ether and benzene, easily so in alcohol and chloroform; with alcoholic potash, it yields a single *β-dinaphthyl-αγ-diketo-βδ-dimethylpiperazine*, crystallising from chloroform in needles, and melting at 268—270°. From the mother liquors of the piperazine, a compound, $C_{11}H_{11}NO_2$, was isolated, analogous to that obtained from the α-naphthylide; this substance is rather more soluble than the α-compound, crystallises in colourless needles, and melts at 191—193°. These compounds are probably formed according to the equation $C_{13}N_{12}NOBr + KOH + H_2O = KBr + C_{11}H_{11}NO_2 + C_2H_4O$. The author is further investigating them.

Derivatives of α-Bromobutyryl, $NXH{\cdot}CO{\cdot}CHBr{\cdot}CH_2{\cdot}CH_3$. — The *anilide* crystallises in needles melting at 98°. It yields with alcoholic potash the diphenyl-αγ-diethyl-βδ-diketopiperazine (m. p. 260°), obtained by Nastvogel from anilidobutyric acid (Abstr., 1890, 1160). The *orthotoluidide* crystallises from hot light petroleum in agglomerated needles melting at 109°, and yields with alcoholic potash two *diorthotolyl-αγ-diketo-βδ-diethylpiperazines*. The *para*-modification forms small prisms melting at 218°, soluble in chloroform, benzene, and alcohol, insoluble in ether and light petroleum. The *anti*-modification forms slightly more soluble prisms melting at 178—180°. The separation of the two isomerides was effected by treatment with water and alcohol. The *paratoluidide* crystallises from alcohol in prisms melting at 92·5°, and with potash yields the two diparatolyl-αγ-diketo-βδ-diethylpiperazines obtained from α-orthotoluidobutyric acid (Abstr., 1892, 1338). The *α-naphthalide* crystallises from alcohol in needles, and melts at 151°; with potash, it yields a crystalline *di-α-naphthyl-αγ-diketo-βδ-dimethylpiperazine* melting at 287—289°, together with *α-ethoxybutyro-α-naphthalide*, $C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}CH(OEt){\cdot}C_2H_5$, which is insoluble in water and light petroleum, and crystallises in needles melting at 79—80°. The *β-naphthalide* forms matted needles melting at 134°, and on treatment with potash yields the *para*-modification of *di-β-naphthyl-αγ-diketo-βδ-diethylpiperazine*, which crystallises in needles, and melts at 306°. By long continued digestion with concentrated alcoholic potash, the para- is converted into the *anti*-modification melting at 246—247°, and crystallising in microscopic prisms. The mother liquors of the para-compound contain *α-ethoxybutyro-β-naphthalido-α-butyro-β-naphthalide*,

$$C_{10}H_7\cdot NH\cdot CO\cdot CHEt\cdot N(C_{10}H_7)\cdot CO\cdot CHEt\cdot OEt,$$

which is insoluble in water and light petroleum, easily soluble in alcohol, ether, &c., crystallises in needles, and melts at 106—110°. The isolation of this compound shows that the formation of the piperazine takes place in two stages.

Derivatives of α-Bromisobutyryl, $NHX\cdot CO\cdot CMe_2Br$.—No piperazine could be obtained from the anilide, α-hydroxy- and α-ethoxy-isobutyric acids only being formed. The *orthotoluidide* crystallises from chloroform in prisms, and melts at 63°. The action of alcoholic potash yielded α-ethoxyisobutyrorthotoluidide and isobutyrorthotoluidide. The *paratoluidide* crystallises from alcohol in prisms, and melts at 90°. With alcoholic potash, it yielded *α-hydroxyisobutyroparatoluidide*, crystallising in cubes, and melting at 132—133°. The *α-naphthalide* crystallises from chloroform in needles melting at 116°. With alcoholic potash, it yielded *α-ethoxyisobutyro-β-naphthalide*, which forms soluble prisms melting at 74—76°. The *β-naphthalide* crystallises from benzene in needles melting at 135°. With alcoholic potash, it yielded *α-hydroxy-* and *α-ethoxy-isobutyro-β-naphthalides*, the former crystallising in plates melting at 157—159°, the latter in needles melting at 50°. Small quantities of *α-ethoxyisobutyro-β-naphthalido-α-isobutyro-β-naphthalide* (m. p. 156—165°) were also obtained. The preceding results show that the isobutyric compounds do not condense to form a diketo-piperazine ring. L. T. T.

Monoketopiperazines. By C. A. Bischoff and C. Trapesonzjanz and others (*Ber.*, **25**, 2931—2940).—The authors have previously described the diphenyl-, diparatolyl-, and diparaethoxyphenyl-ketopiperazines, which were obtained by heating the secondary bases with chloracetic acid in the presence of dry sodium acetate. Kaminsky has now similarly obtained *di-β-naphthylketopiperazine*,

$$C_{10}H_7\cdot N<\begin{matrix}CH_2\cdot CH_2\\CO\cdot CH_2\end{matrix}>N\cdot C_{10}H_7.$$

It crystallises in colourless, hexagonal plates melting at 222—224°. It is sparingly soluble in alcohol, chloroform, acetone, light petroleum, and benzene, insoluble in water and hydrochloric acid. Long-continued boiling with alcoholic potash splits the ring nucleus with formation of the corresponding *acid*, but the acid passes so readily back into the piperazine that it could not be obtained in a state of purity. *Diphenyl-α-keto-β-methylpiperazine*, $NPh<\begin{matrix}CH_2—CH_2\\CO\cdot CHMe\end{matrix}>NPh$, prepared by Klein, crystallises from benzene in glistening, white, quadratic plates and melts at 137—138°. The corresponding *acid* melts at 83°, and passes into the piperazine at 120° with partial further decomposition. *Diparatolyl-α-keto-β-methylpiperazine* crystallises in flat prisms melting at 117—118°. A second compound, of very similar, if not identical, composition, and most probably a geometric isomeride, was formed at the same time. *Diphenyl-α-ethyl-β-ketopiperazine* crystallises from light petroleum in prisms melting at 93—94°. It is easily soluble in chloroform, carbon bisulphide, benzene, alcohol, and acetic acid. The corresponding *acid* melts at about 40°, and at

120—130° is reconverted into the piperazine. *Diparatolyl-α-ethyl-β-ketopiperazine*, $C_6H_4Me\cdot N<\begin{matrix}CH_2-CH_2\\CHEt\cdot CO\end{matrix}>N\cdot C_6H_4Me$, forms soluble, crystalline aggregates melting at 98—99·5°. The acid is so unstable that it could not be obtained pure. *Diphenyl-α-dimethyl-β-ketopiperazine*, $NPh<\begin{matrix}CH_2\cdot CH_2\\CMe_2\cdot CO\end{matrix}>NPh$, or possibly

$$NPh<\begin{matrix}CH_2\text{———}CH_2\\CH_2\cdot CHMe\cdot CO\end{matrix}>NPh$$

(from α-bromoisobutyric acid), forms thin, colourless plates, crystallising at 116°. Long boiling with alcoholic potash yields the corresponding *acid*. *Diparatolyl-α-dimethyl-β-ketopiperazine*, $C_{18}H_{21}N_2O$, crystallises in prisms melting at 129—130°. *Diorthotolylketopiperazine* could not be obtained by heating the diamine and bromo-acid with sodium acetate; it was, however, obtained by Walden's method, by reducing the diketopiperazine with tin and fuming hydrochloric acid, or, preferably, with zinc-dust and acetic acid. It crystallises in prisms melting at 79°. *α-Naphthylketopiperazine* was similarly prepared from the corresponding diketopiperazine. It melts at 92°.

The monoketopiperazines are very stable towards nascent hydrogen, the reduction of the more highly oxidised compounds not going beyond the monoketopiperazines. L. T. T.

Piperazine Group. By C. A. Bischoff and others (*Ber.*, **25**, 2940—2956).—By the reduction of the derivatives obtained by the action of nitrous acid on the piperazines (Abstr., 1890, 1333), diamido-piperazines are formed. *Diamido-diorthotolylpiperazine*, $NH_2\cdot C_6H_3Me\cdot N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N\cdot C_6H_3Me\cdot NH_2$, was obtained by Reinus by reducing, by means of tin and hydrochloric acid, the nitration product of diorthotolylpiperazine. It forms intensely yellow, crystalline aggregates melting at 195—196°. It is soluble in alcohol, ether, and benzene, and in dilute acids. *Diamidodiparatolylpiperazine*, similarly prepared by Hoppen, is intensely yellow and crystalline, and melts at 193°. The *hydrochloride* melts at 288—292°; the *sulphate* forms silky needles, darkening at 204—210°, and melting at 217—218°. The base oxidises readily when exposed to the air, especially in the presence of moisture.

Taken in the light of the non-reducibility by nascent hydrogen of the monoketopiperazines (see preceding abstract), the formation of these compounds from the diketopiperazine nitration products proves that, in these latter compounds, the nitration has caused the introduction of the nitro-group into the phenyl nuclei.

No satisfactory results could be obtained by the oxidation of the piperazines, which thus show a marked difference from the ketopiperazines.

Considering the analogy of the piperazines to the hexamethylenes, from which v. Baeyer has obtained geometric isomerides, the former substances were subjected to various modes of treatment, in the hope of producing analogous isomerides. No such geometric isomerides were, however, obtained, but, when heated with a saturated solution of

hydrogen chloride in glacial acetic acid, acetylethylenediamines were obtained.

Di-α-naphthyl-αβ-diketopiperazine, $C_{10}H_7{\cdot}N{<}\begin{matrix}CH_2{\cdot}CH_2\\CO\text{—}CO\end{matrix}{>}NC_{10}H_7$, was prepared by Zabko-Potopowicz from ethylenedinaphthylamine and oxalic acid. It forms small, colourless plates melting at 281—283°. Potash converts it into the corresponding unstable acid, which gradually passes back into the piperazine at ordinary temperatures, and at once if heated to 127—150°. *Di-β-naphthyl-αβ-diketopiperazine*, prepared by Kochanowski, forms colourless needles melting above 360°. It is soluble in boiling aniline, nitrobenzene, and acetic anhydride, insoluble in most other solvents. At the same time, a small quantity of a yellow powder melting at 200—202° was formed, but it was not further investigated.

Attempts to obtain piperazine derivatives by the action of phosphoric oxychloride on mixtures of anilides and hydroxy-acids proved futile. With tartaric and malic acids, however, closely allied compounds were obtained. From tartaric acid, a compound melting at 234° was formed, which the author believes to be $\begin{matrix}CO\text{—}CH{\cdot}NPh\\|\quad\quad|\\NPh{\cdot}CH{\cdot}CO\end{matrix}$, already obtained (Abstr., 1886, 551, 698, 791) from aniline and dibromosuccinic, bromomaleïc, or bromofumaric acid. The investigation of this reaction is being continued.

The author also gives a *résumé* of the work done on the piperazine group up to the present. L. T. T.

Organic Bases in the Juice of Flesh. By G. S. Johnson (*Proc. Roy. Soc.*, **50**, 287—302). The aqueous extract expressed from the flesh of a healthy cow was treated with mercuric chloride solution, filtered, and the precipitate decomposed by hydrogen sulphide. After filtering, the solution, on spontaneous evaporation over sulphuric acid, deposited *sarcous creatinine hydrochloride* in crystals isomorphous but not identical with those of urinary creatinine hydrochloride. On digesting the aqueous solution of the new salt with lead hydroxide, *sarcous creatinine* is obtained; it forms anhydrous, tabular crystals if prepared in the cold, but, on evaporating its solution at 60°, it separates in efflorescent needles, isomorphous with urinary creatinine. It is soluble in 490·2 parts of alcohol (sp. gr. 0·800) at 13·7°. The *platinochloride*, $(C_4H_7N_3O)_2,H_2PtCl_6,2H_2O$, forms yellow crystals, which lose their water at 100°, and dissolve in 22·6 parts of water at 15°. The *aurochloride*, $C_4H_7N_3O,HAuCl_4$, forms glistening, yellow plates; it is soluble in ether, and the solution, on spontaneous evaporation, deposits a mixture of the hydrochloride and auric chloride. Sarcous creatinine (9 mols.) reduces cupric oxide (4 mols.) in boiling alkaline solution. The properties of this base differ very considerably from those of urinary creatinine.

The excess of mercuric chloride is very slowly, but completely, removed from the mother liquor, remaining after separation of the creatinine compound, by the action of lead hydroxide. From experiments on the amount of creatine contained in the aqueous flesh

extract, in which germ action was arrested by the addition of mercuric chloride at various periods after death, the author is inclined to conclude that creatine is not originally present in fresh muscle substance, but is a product of bacterial action on some constituent of the flesh; the source of the creatine is probably sarcous creatinine or some closely allied substance. Sarcous creatinine, although probably a true educt, may result from the prolonged action of the mercuric chloride on some similar substance.

Contrary to the general belief, creatine is acted on by mercuric chloride; an aqueous solution of the two substances slowly deposits creatinine mercuric chloride. That this reaction does not occur in treating the flesh extract with mercuric chloride, as described above, is assured by the fact that the creatinine so obtained is not sarcous creatinine, but closely resembles urinary creatinine prepared by Liebig's method. W. J. P.

Conversion of Cinchona Alkaloïds into Isomerides. By Z. H. Skraup (*Ber.*, **25**, 2909—2912).—Königs has shown (Abstr., 1887, 1123, and 1891, 1010) that when halogen additive derivatives of cinchonine are heated with alcoholic potash, cinchonine is re-formed, together with an isomeride, isocinchonine. The author, working with Pum and Neumann on the hydriodides of various cinchona alkaloïds, has found that in many cases little or none of the original alkaloïd is re-formed, but that new isomeric bases are produced. This is especially the case when the decomposition of the halogen derivative is effected by means of silver nitrate in place of alcoholic potash. Cinchonide hydriodide yields with alcoholic potash *β-cinchonidine*, melting at 244°; its *sulphate*, *hydrochloride*, and *nitrate* are non-crystallisable, whilst its *oxalate* and *normal tartrate* are crystalline. In other respects it closely resembles cinchonidine. With silver nitrate, on the other hand, cinchonidine hydriodide yields *γ-cinchonidine*, melting at 238°, and giving salts of which only the *acid tartrate* is crystallisable.

Cinchonine hydriodide treated with silver nitrate yields some isocinchonine, but mainly *β-cinchonine*, sparingly soluble in ether, melting at 250—252°, and giving a characteristic *sulphate*,

$$(C_{19}H_{22}N_2O)_2H_2SO_4 + 2H_2O,$$

crystallising in matted needles. Isocinchonine and β-cinchonine give hydriodides, which in physical properties both closely resemble that of cinchonine. But the β-hydriodide, when treated either with alcoholic potash or silver nitrate, yields β-cinchonidine, with only very little isocinchonine, whilst the iso-hydriodide yields with potash only very little isocinchonine, a new isomeride, *γ-cinchonine*, being the chief product. This melts at 230—235°, and gives an anhydrous *sulphate* $(C_{19}H_{22}N_2O)_2H_2SO_4$, crystallising in needles. It is possible that these β- and γ-cinchonines may be identical with the alkaloïds obtained by Jungfleisch and Leger by heating cinchonine with sulphuric acid.

When quinine hydriodide is heated with alcoholic potash, about equal proportions of quinine, *pseudoquinine*, and *nichine* are produced. If silver nitrate is used in place of potash, the same products are formed, but nichine predominates. *Pseudoquinine*, $C_{20}H_{24}N_2O_2$, crystal-

lises easily, melts at 191°, and is lævorotatory. The *hydrochloride*, $C_{20}H_{24}N_2O_2,HCl$, the *normal nitrate*, and a *basic nitrate*,

$$(C_{20}H_{24}N_2O_2)_2,HNO_3,$$

are sparingly soluble and crystallise easily. *Nichine*, $C_{19}H_{24}N_2O_2$ (or, possibly, $C_{19}H_{22}N_2O_2$), crystallises easily and yields well crystallised *acid hydrochloride*, *hydriodide*, and *sulphate* sparingly soluble in alcohol and water, and an *oxalate* (with 2 mols. oxalic acid), almost insoluble in boiling alcohol. The formation of nichine probably takes place according to the reaction

$$C_{20}H_{24}N_2O_2 + 2H_2O = C_{19}H_{24}N_2O_2 + H{\cdot}COH + H_2O,$$

and an aldehydic compound was found to be present in the products of reaction.

With hydriodic acid, pseudoquinine yields a hydriodide, probably identical with that formed from quinine. Nichine forms a *hydriodide*, $C_{19}H_{24}N_2O_2,3HI$, differing entirely from the corresponding derivative of quinine. When decomposed by alcoholic potash, it yields mainly regenerated nichine, together with a little of a new isomeride, *isonichine*. The authors believe Lippmann and Fleissner's isoquinine (Abstr., 1892, 82) was a mixture of pseudoquinine and nichine.

An aldehydic substance reducing silver nitrate was also found in the distillates from the decomposition of the hydriodides of cinchonidine, and it is, therefore, possible that alkaloïds containing one less carbon atom than the originals were also formed in these reactions. (Compare also Abstr., 1891, 1517; 1892, 83, 640, and 1363.)

L. T. T.

Coca Leaves. By O. Hesse (*Annalen*, **271**, 180—228).—In this paper, the author gives a short account of the various substances which have been obtained from coca leaves; with a few exceptions, most of the compounds here referred to have been previously described by the author (Abstr., 1889, 751, and *Pharm. J. Trans.* [3], **21**, 1109, 1120); Liebermann (Abstr., 1890, 76, 494; 1891, 1265, 1520); Einhorn, Giesel, and others.

Cinnamylcocaïne hydrochloride, $C_{19}H_{23}NO_4,HCl + 2H_2O$, crystallises from water, in which it is readily soluble, in lustrous plates, loses its water at 66°, and melts at 176°; its specific rotatory power in aqueous solution is $[\alpha]_D = -104{\cdot}1$. The *platinochloride*, $(C_{19}H_{23}NO_4)_2,H_2PtCl_6$, crystallises in small needles, and is moderately easily soluble in boiling water. The *aurochloride*, $C_{19}H_{23}NO_4,HAuCl_4$, crystallises in small, yellow needles, and melts at 156°. The *methiodide*, $C_{19}H_{23}NO_4,MeI$, crystallises from alcohol in small, colourless needles; the corresponding *methochloride* is a crystalline substance, readily soluble in water and alcohol, but insoluble in ether.

The molecular formula of homococaïc acid, determined in glacial acetic acid solution, was found to be $C_9H_8O_2$. This acid melts at 150°, and dissolves freely in alcohol, ether, chloroform, glacial acetic acid, and hot water, but is only sparingly soluble in light petroleum and cold water; it is only slowly oxidised by a warm solution of potassium permanganate. A number of its salts were prepared and analysed,

but they are all amorphous, ill-characterised compounds. The *nitro*-derivative, $C_9H_7O_2{\cdot}NO_2$, prepared by warming the acid with nitric acid of sp. gr. 1·52, crystallises from dilute acetic acid in yellowish needles, melts at 226°, and is readily soluble in alcohol and glacial acetic acid, but more sparingly in chloroform, ether, and boiling water.

β-Cocaïc acid, $C_{18}H_{16}O_4$, is formed when homococaïc acid is heated for a long time with concentrated hydrochloric acid, or fused with potash; it crystallises from boiling water in long, colourless needles, melts at 189°, and is readily soluble in glacial acetic acid, alcohol, and chloroform, but more sparingly in benzene, and almost insoluble in light petroleum; its molecular weight was determined in glacial acetic acid solution, with results in accordance with the molecular formula given above. It is only very slightly acted on by potassium permanganate. The *potassium* salt crystallises in lustrous prisms, and is readily soluble in cold water. The *copper* salt, $C_{18}H_{14}O_4Cu + 2H_2O$, is a green, crystalline compound, and loses its water at 160°, becoming dark-blue. The *silver* salt, $C_{18}H_{14}O_4Ag_2$, is stable in the light. The *methyl* salt, $C_{18}H_{14}O_4Me_2$, is a mobile oil. The *dinitro*-derivative, $C_{18}H_{14}O_4(NO_2)_2$, prepared by treating the acid with concentrated nitric acid, crystallises from glacial acetic acid in pale yellow prisms, melts at 252°, and is readily soluble in alcohol, chloroform, glacial acetic acid, and ether, but more sparingly in water.

β-Isococaïc acid or δ-truxillic acid (compare Liebermann, Abstr., 1889, 1194), prepared from isococaïc acid in like manner, has the molecular formula $C_{18}H_{16}O_4$; it melts at 172°, not at 174°, as stated by Liebermann. The *barium* salt, $C_{18}H_{14}O_4Ba + 4H_2O$, crystallises in short, lustrous prisms; the *copper* salt crystallises with 2 mols. H_2O. The *dinitro*-derivative, $C_{18}H_{14}O_4(NO_2)_2$, crystallises from dilute acetic acid in small, almost colourless prisms, melts at 226°, and is very readily soluble in alcohol and ether, but almost insoluble in benzene.

Benzoylpseudotropeïne methiodide, $C_{15}H_{19}NO_2$,MeI, forms colourless crystals, and is moderately easily soluble in hot, but only sparingly in cold, alcohol. The corresponding *methochloride*, $C_{15}H_{19}NO_2$,MeCl, crystallises in colourless needles or prisms; its *platinochloride*,

$$(C_{15}H_{19}NO_2,MeCl)_2,PtCl_4 + 2H_2O,$$

forms small, orange needles, and is sparingly soluble in cold water; its *aurochloride*, $C_{15}H_{19}NO_2$,MeCl,$AuCl_3$, is a yellow, crystalline compound, sparingly soluble in cold water.

Pseudotropine methiodide, $C_8H_{15}NO$,MeI, crystallises from hot water in small, colourless, rhombic crystals, and melts at 270°. The *methochloride*, $C_8H_{15}NO$,MeCl, forms compact, rhombic crystals, and is readily soluble in water, but only sparingly in alcohol; its *platinochloride*, $(C_8H_{15}NO,MeCl)_2,PtCl_4$, separates from hot water in crystals, and melts at 216°.

Palmityl-β-amyrin, $C_{46}H_{80}O_2$, occurs in Trujillo coca; it melts at 75°, dissolves freely in ether, chloroform, light petroleum, hot alcohol, and acetone, and has a specific rotatory power $[\alpha]_D = 54{\cdot}5°$ in alcoholic solution; on hydrolysis, it yields palmitic acid and β-amyrin. The wax obtained from the broad-leaved coca of Peru and Bolivia consists of palmityl-β-amyrin and cerotone, $C_{25}H_{50}O$, melting at 66°; the wax

from Java coca seems to consist of palmityl-β-amyrin, cerotone, ceryl cerotate, myristyl-β-amyrin, and a substance which the author names hydroxycerotic acid.

Hydroxycerotic acid, $C_{27}H_{54}O_3$, melts at 82°, and dissolves freely in hot alcohol and light petroleum, but is only very sparingly soluble in cold ether.

Cerotolic acid, $C_{27}H_{52}O_2$, is formed when hydroxycerotic acid is heated at 100° with acetic anhydride for eight days; it crystallises in short prisms, and is moderately easily soluble in cold ether and light petroleum. F. S. K.

Echinochrome, a Respiratory Pigment. By A. B. GRIFFITHS (*Compt. rend.*, **115**, 419—420).—The echinochrome discovered by MacMunn in several echinoderms is a respiratory pigment existing in two states of oxidation. It has the empirical composition $C_{102}H_{99}N_{12}FeS_2O_{18}$, is partially soluble in water or alcohol, and dissolves readily in chloroform, benzene, or carbon bisulphide. When boiled with inorganic acids, it yields hæmatoporphyrin, hæmochromogen, and sulphuric acid.

Echinochrome in some respects is analogous to hæmoglobin and chlorocruorin, and is probably a respiratory pigment in a low state of development. The respiratory pigments of the lower animals not only carry oxygen to the tissues, but also retain oxygen until they are themselves taken up by the tissues in the processes of metabolism. This is why hæmocyanin, chlorocruorin, pinnaglobin, achroglobin, and echinochrome are much more stable than hæmoglobin. C. H. B.

Hermerythrin, a Respiratory Pigment contained in the Blood of certain Worms. By A. B. GRIFFITHS (*Compt. rend.*, **115**, 669—670).—Hermerythrin, described by Krukenberg, was extracted from the blood of *Sipunculus* and analysed. The results lead to the empirical formula $C_{427}H_{761}N_{133}FeS_2O_{153}$. The pigment exists in two states, oxyhermerythrin, which is red, and reduced hermerythrin, which is brown. The ash of the blood of *Sipunculus* has the composition: Fe_2O_3, 0·13; CaO, 3·00; MgO, 1·65; K_2O, 5·02; Na_2O, 44·31; P_2O_5, 4·78; SO_3, 2·86; Cl, 38·25. C. H. B.

Fractional Heat Coagulation. By R. T. HEWLETT (*J. Physiol.*, **13**, 493—512).—In determining the coagulation temperatures of proteïds, an oil-bath has some advantages over a water-bath. There is no need to make a distinction between temperature of opalescence and temperature of coagulation (formation of flocculi). Both take place at the same temperature if the rate of heating is sufficiently slow. A slow rate of heating is essential for obtaining correct coagulation temperatures, especially when the solution is dilute. Prolonged heating does not alter the coagulation temperature of a proteïd. Very dilute solutions of a proteïd may be prevented from coagulating by a comparatively small excess of acid or alkali. The phenomena of fractional heat coagulation are not due, as Haycraft and Duggan state, to the effects of dilution for (*a*) dilution, if the rate of heating be

sufficiently slow, does not raise the coagulation temperature, and (5) in fractionating, the rise in the coagulation temperature is out of all proportion to the dilution. A striking experiment confirmatory of the foregoing was the following: white of egg solution was heated to the temperature at which coagulation first occurred; this was filtered off; the filtrate coagulated at a higher temperature, showing the presence of a second proteïd with a higher coagulation temperature, as Halliburton would say; this view was confirmed by concentrating the filtrate, and thus dilution of the solution was obviated. The filtrate, however, still coagulated at the higher temperature, although its concentration was, so far as proteïd in it was concerned, as great as in the original liquid.

White of egg is a mixture of at least three proteïds, one of which is a globulin coagulating at 56°.

The opinion is expressed that it would be advisable to decide on some standard conditions (solvent, &c.) under which to determine coagulation temperatures. W. D. H.

Rotatory Power of Fibroïn. By L. Vignon (*Compt. rend.*, 115, 442—444).—The author has already shown that an acid solution of fibroïn from silk acts on polarised light (Abstr., 1892, 254, 265). If a solution of fibroïn in hydrochloric acid is gradually neutralised with sodium hydroxide, an abundant, white precipitate is formed near the point of neutrality, but precipitation is never complete. The precipitate, when freshly prepared, is soluble in sodium hydroxide.

If, however, 20 c.c. of the hydrochloric acid solution of fibroïn is mixed with 100 c.c. of ethyl alcohol of 95°, the fibroïn is completely precipitated without alteration of properties. When dried by exposure to air, its sp. gr. is 1·32, and it is insoluble in cold dilute sodium hydroxide solution, but dissolves in concentrated hydrochloric acid, and is decomposed by warm concentrated sodium hydroxide solution. The precipitated fibroïn has a rotatory power $[\alpha]_j = -43·2°$, practically identical with that of the original fibroïn, and it exerts the same absorptive action on colouring matters. C. H. B.

Respiratory Globulin in the Blood of Chitons. By A. B. Griffiths (*Compt. rend.*, **115**, 474—475).—The blood of chitons has a yellow colour, but the pigment is a luteïn or lipochrome, and has no respiratory function. The blood, however, contains a colourless respiratory globulin with the same function as hæmoglobin, hæmocyanin, pinnaglobin, and chlorocruorin, but it contains no metal. Its empirical formula is $C_{621}H_{814}N_{175}SO_{169}$, and 100 c.c. absorb 120 c.c. of oxygen and 281 c.c. of carbonic anhydride at 0° and 760 mm. When dissolved in a dilute solution of magnesium sulphate, its specific rotatory power $[\alpha]_D = -55°$. Even when oxygenated, it is colourless, and the author calls it *β-achroglobin* in order to distinguish it from achroglobin, which exists in the blood of *Patella*. C. H. B.

Organic Chemistry.

Hydration of Ethylenic Hydrocarbons. By S. MIKLASHEFFSKY (*J. Russ. Chem. Soc.*, **22**, 495—506).—As very dilute solutions of mineral acids can bring about the addition of the elements of water to unsaturated hydrocarbons of the ethylene series, the author has investigated the capability of the feebler organic acids to effect the same addition. He employed, principally, solutions of oxalic acid of 5, 8, and 10 per cent. concentration.

Isobutylene prepared from isobutyl iodide was led into soda water bottles containing the acid solution, and immersed in a freezing mixture. When a sufficient quantity of the hydrocarbon had condensed, the bottles were closed by an india-rubber stopper tied firmly down, and were then left lying in a horizontal position, some at the ordinary temperature, and some at about 40°. After the lapse of a month, it was found that the layer of hydrocarbon had completely disappeared in the bottles which had been heated. These were then opened, their contents neutralised with potassium carbonate, and the colourless oil which separated, distilled off on the water-bath. This oil, when dried with fused potash and boiled with baryta, distilled at 82·5—83°, solidifying in the receiver to prismatic crystals, which melted at about 25°. From these data, and the strong camphoric odour of the substance, it would appear to be trimethylcarbinol. The same reaction occurs at the ordinary temperature, but the time required for its completion is about two and a half months.

Commercial amylene is very slowly attacked at the ordinary temperature by solutions of oxalic acid, but at 100°, the addition of water goes on more rapidly, a considerable quantity of the hydrocarbon disappearing after four days' heating. The aqueous solution was found to contain dimethylethylcarbinol, boiling at 101·5°. At the ordinary temperature, the same substance was formed in the course of a year. Experiments with similar results were also made on the mixture of the two isomeric amylenes, prepared by the action of alcoholic potash on dimethylethylcarbinyl iodide. The alcohol thus prepared has a sp. gr. = 0·8268 at 0°/0°, and 0·8103 at 21·5°/21·5°. The corresponding chloride boiled at 86—87°. Acetic and formic acids behave similarly to oxalic acid, only their action is much slower, acetic acid being the least active of the three.

Normal propylethylene did not take up the elements of water under the above conditions.

On heating tetramethylethylene from the iodide of dimethylisopropylcarbinol with the acid for 2—3 weeks at 100°, it gave the original alcohol boiling at 117—119° under a pressure of 765 mm.

Diisobutylene remained unchanged on similar treatment.

The organic acids are thus active in effecting the conversion of unsaturated hydrocarbons into tertiary alcohols precisely in the same way as the strong mineral acids, from which they differ, however, in not simultaneously causing polymerisation of the hydrocarbons.

J. W.

Preparation of Acetylene. By L. Maquenne (*Compt. rend.*, **115**, 558—561).—Barium carbide is easily obtained in large quantities and in a pure condition in the following manner. 26 grams of precipitated barium carbonate is mixed with 10·5 grams of powdered magnesium and 4 grams of retort carbon previously heated in a platinum crucible, and the mixture is placed in an iron bottle of about 700 c.c. capacity, to the neck of which is fitted an iron tube 30 cm. long and 2 cm. in diameter; on heating the bottle to redness, an energetic reaction soon takes place, with projection of sparks from the end of the tube. When this ceases, the end of the tube is closed, and the bottle is cooled as rapidly as possible. The product is a mixture of magnesium oxide with 38 per cent. of barium carbide, a small excess of carbon, and a trace of cyanide. It is a light, porous, friable, amorphous mass of a grey colour. It does not alter in dry air, and is not attacked by chlorine or gaseous hydrogen chloride in the cold. Acid anhydrides, acid chlorides, and even phosphorus pentachloride, have no action on it at 100°; at a red heat, it burns with vivid incandescence in air, sulphur vapour, chlorine, or hydrogen chloride.

When treated with water, alcohol, or, as a rule, any compound containing hydroxyl, barium carbide yields acetylene at the ordinary temperature. If water is allowed to fall on the carbide drop by drop, a regular current of acetylene is obtained containing only 2 to 3 per cent. of hydrogen, and no appreciable trace of any other hydrocarbon, the yield being about two-thirds of that calculated from the weight of magnesium originally employed.

By passing this acetylene through a long glass tube heated to dull redness, the author has obtained in one day several grams of synthetic benzene. C. H. B.

Action of Bromine on Ethyl Chloride and on certain Butane Derivatives. By V. Meyer and P. Petrenko-Kritschenko (*Ber.*, **25**, 3304—3310; compare Meyer and Müller, Abstr., 1892, 1414).—Ethyl chloride is heated on the water-bath in a sealed tube with iron wire and bromine; the product consists of ethylene bromide (66 per cent.) and ethyl bromide (14·5 per cent.); the chlorine is, therefore, displaced by the bromine, and the ethyl bromide then undergoes further substitution in the usual manner.

By the action of bromine on butyl bromide, Meyer and Müller obtained (*loc. cit.*) a compound which they believed to be pseudobutylene bromide, CHBrMe·CHBrMe; on heating it with lead oxide and water in a sealed tube at 150°, ethyl methyl ketone is formed, and their supposition is thus shown to be correct. It is probable that in the process of bromination, normal butyl bromide is converted into secondary butyl bromide.

1 : 1-Dichlorobutane, prepared from phosphoric chloride and normal butaldehyde, is also decomposed by the action of water and lead oxide, butaldehyde being regenerated. J. B. T.

Catalytic Action of Aluminium Chloride on Ethereal Silicates. By H. N. Stokes (*Amer. Chem. J.*, **14**, 438—454).—Aluminium chloride dissolves quietly in ice-cold ethyl trichlorosilicate,

$SiCl_3{\cdot}OEt$, but on allowing the temperature to rise, a violent reaction sets in, and ethyl chloride is evolved. The aluminium chloride, of which a trace is enough to determine the reaction, may afterwards be distilled unchanged from the residue, which has the approximate composition $SiOCl_2$, although it is probably a complex mixture of silica with various oxychlorides of silicon. It is possible that unstable intermediate compounds such as $SiO<^{O}_{O}>AlCl$ and $Cl_2AlO{\cdot}SiO{\cdot}OAlCl_2$, of gradually increasing complexity, are formed by the assumption of aluminium chloride, rearrangement of the complex, and elimination of the chlorine, and a number of equations are given in illustration of this view, which is borne out, moreover, by the gradual increase in viscosity of the liquid during the course of the reaction. The rearrangement may be attributed to the superior affinity of silicon over that of aluminium for oxygen. Further evidence in favour of the existence of complex aluminium chlorosilicates and silicon oxychlorides is furnished by the interaction of aluminium chloride with ethyl monochlorosilicate. The silicate, like its trichlorinated analogue, is completely decomposed under the influence of a very small quantity of the chloride, ethyl chloride and ether being formed, but the aluminium chloride remains combined with the silica, since, as the hypothesis points out, there is not enough chlorine in the silicate to complete the regeneration. But as the proportion of aluminium chloride increases, less ether is formed and more ethyl chloride, and when the ratio of silicon to aluminium is as 3 : 2, the whole of the chlorine passes into the ethyl chloride, and no ether is formed at all. Any excess of the chloride over this amount may be sublimed unchanged at the end of the operation. With ethyl orthosilicate, the reaction is of a different character. Since there is no chlorine in it, there is no regeneration of aluminium chloride, and hence the amount of change is strictly proportional to the amount of the latter. The formation of ether is probably due to the breaking-down of intermediate ortho-compounds such as $(EtO)_2SiO_2AlCl$, the ortho-acids of silicon, like those of carbon, seeming to rise to their highest basicity only in their ethereal combinations. JN. W.

Alcohols in Fusel Oil. By R. C. SCHÜPPHAUS (*Chem. Centr.*, 1892, ii, 206; from *J. Amer. Chem. Soc.*, **14**, 45—60).—In order to analyse fusel oil, it must be completely dried with anhydrous potassium carbonate, and then repeatedly fractionated. In four samples were found water, 14—23; normal propyl alcohol, 5·7—14·5; isobutyl alcohol, 11·0—25·2; fermentation amyl alcohol, 7·0—36·8; residue, boiling above 132°, probably a mixture of amyl ethers, 0·5—2·0 parts per cent. Rabuteau's statement that isopropyl alcohol is contained in fusel oil is probably incorrect. C. F. B.

Levulan. By E. O. v. LIPPMANN and O. HAHN (*Ber.*, **25**, 3216).—The authors, having obtained another sample of levulan, have repeated Lippmann's experiments on its oxidation with nitric acid. They find that no mucic acid is formed, oxalic acid being the chief product. Its behaviour on oxidation is, therefore, in consonance with its close relationship to levulose. L. T. T.

Dulcitol. By E. O. v. LIPPMANN (*Ber.*, **25**, 3216—3218).—The author has obtained dulcitol from the products of the yeast fermentation of a Mozambique cane sugar. During his work on this subject, he observed a peculiar mucous fermentation in a sample of calcium mucate, pyrroline being found amongst the products. L. T. T.

Sorbitol. By E. O. v. LIPPMANN (*Ber.*, **25**, 3218—3220).—The author has discovered small quantities of sorbitol in a sample of molasses from mixed sugars of various sources. L. T. T.

Agavose. By G. MICHAUD and J. F. TRISTAN (*Amer. Chem. J.*, **14**, 548—550).—The *Agave Americana* is extensively grown in Mexico for the sake of the juice of the stalk, from which a fermented intoxicating drink called *pulque* is made. The substance yielding the alcohol is a sugar, which may be isolated by the following process:—The juice is first treated with alcohol (2 vols. 90 per cent.) and filtered; basic lead acetate is next added to the solution, which is again filtered, the excess of lead being subsequently removed from the filtrate by means of hydrogen sulphide; the clear liquid is now evaporated to a syrup under diminished pressure, and left to crystallise in a warm place.

Agavose, $C_{12}H_{22}O_{11}$, is an inactive sugar, which reduces alkaline copper tartrate, and yields a lævogyrate sugar ($[\alpha]_y = -14{\cdot}43$) on inversion. It is oxidised by nitric acid, but not to mucic acid, and forms a soluble lime compound, which is precipitated by alcohol or by heating. JN. W.

Effect of Boiling with Water on Cane Sugar and Raffinose. By J. WEISBERG (*Chem. Centr.*, 1892, ii, 458; from *Österr.-ungar. Zeit. Zuck.-Ind. Landw.*, **21**, 438—442).—An aqueous solution of pure cane sugar may be heated for an hour at 100—105° without any change taking place. After heating for several hours, a slight decrease of rotatory power can be observed, and the solution reduces Fehling's solution to some extent. The same is the case if the sugar solution is made alkaline and traces of inorganic or organic salts added, or if lime is present.

Raffinose is even less affected than cane sugar; the boiling with water must be continued for 15 hours before any decrease of rotatory power can be detected, and even then there is hardly any apparent reduction of Fehling's solution. C. F. B.

Metaldehyde and Paraldehyde. By J. TROEGER (*Ber.*, **25**, 3316—3317).—A sample of pure metaldehyde which had been kept for 10 years protected from direct sunlight was found to have undergone partial conversion into acetaldehyde and paraldehyde, the latter predominating. A conversion of paraldehyde into acetaldehyde under like circumstances was also observed. A. R. L.

Thiocyanacetone. By A. HANTZSCH (*Ber.*, **25**, 3282—3286).—A refutation of Tcherniac's criticisms (Abstr., 1892, 1425).

Substitution in Aliphatic Acids. By V. MEYER (*Ber.*, **25**, 3310—3312).—The author refers to the fact that α-halogenated

fatty acids are always obtained by direct substitution, and that this process was believed to be analogous to the formation of dihalogenated substituted paraffin derivatives, thus: $CHMe{:}COOH$ and CH_2MeCl gave $CHMeCl{\cdot}COOH$ and $CHMeCl_2$ respectively. It has, however, been shown by the author and Müller that in the case of paraffin hydrocarbons the second halogen atom links itself to the carbon atom adjacent to that to which the first halogen atom is linked; but the analogy in the substitution of the two classes of compounds is still maintained, as is readily perceived from a comparison of the substituted acid chlorides and substituted hydrocarbons:—$CH_3{\cdot}CH_2Cl$ and $CH_3{\cdot}COCl$ give $CH_2Cl{\cdot}CH_2Cl$ and $CH_2Cl{\cdot}COCl$; $CH_2Me{\cdot}CH_2Cl$ and $CH_2Me{\cdot}COCl$ give $CHMeCl{\cdot}CH_2Cl$ and $CHMeCl{\cdot}COCl$ respectively; the hydroxyl group in the acids is, therefore, the negative group, and plays the same part as the chlorine atom in the substituted hydrocarbons. J. B. T.

Method of preparing Brominated Fatty Acids. By P. Genvresse (*Bull. Soc. Chim.* [3], **7**, 364—366).—Auger and Béhal (Abstr., 1890, 234) have prepared monochloracetic acid by passing chlorine into boiling glacial acetic acid in the presence of sulphur.

An almost theoretical yield of monobromacetic acid is obtained by gradually adding rather more than the calculated quantity of bromine to a mixture of boiling glacial acetic acid with 5 per cent. of sulphur; the flask containing the mixture should be fitted with a reflux condenser, having a wide tube. Dibromacetic acid is prepared by continuing the addition of bromine to the monobromo-derivative, which may be kept at about 150°. α-Bromopropionic acid is prepared in the same manner (compare Lepercq, next abstract), as is also α-bromobutyric acid. A. R. L.

Action of Alkali Nitrites on Alkyl Salts of Brominated Fatty Acids. By G. Lepercq (*Bull. Soc. Chim.* [3], **7**, 359—361).—Steiner has shown that when a mixture of ethyl chloracetate and potassium nitrite is gently heated, gaseous products and potassium ethyl oxalate are formed; the author states that a nitrogenous compound is also produced.

α-Bromopropionic acid is first prepared by gently heating a mixture of propionic acid (125 grams), bromine (310 grams), and sulphur (2·5 grams) in a reflux apparatus for two hours (compare preceding abstract), and is then converted into the ethyl salt by dissolving it in absolute alcohol, and heating the solution with 5 per cent. of sulphuric acid in a reflux apparatus for two hours. When ethyl α-bromopropionate is heated on the water-bath with its own weight of alcohol and sodium nitrite (2 mols.), hydrogen cyanide, nitrogen, carbonic anhydride, and a little nitric oxide are evolved. The alcoholic liquid is filtered, evaporated on the water-bath, and the residue poured into water, when a red liquid, which cannot be distilled even under diminished pressure, is precipitated, whilst on evaporating the aqueous portion, in a partial vacuum, a compound crystallising in needles is isolated. Both substances contain nitrogen, and are under investigation. Ethyl α-bromobutyrate reacts in like manner with sodium nitrite. A. R. L.

Ethyl Acetoacetate and Ethyl Salicylate. By P. C. Freer (*Amer. Chem. J.*, **14**, 407—422; compare Abstr., 1891, 1181).—The author controverts the conclusion which Nef (Abstr., 1892, 140) draws from the observation that an additive product is formed previous to the separation of the sodium halide in the action of alkyl halides on ethyl acetoacetate. If ethyl acetoacetate is, in reality, ethyl β-hydroxycrotonate, as Nef contends, it contains the same grouping as ethyl salicylate, and the sodium compound of the latter should, therefore, form similar additive compounds. But it does not do so, for the substituting radicle is united to the molecule by oxygen, as is proved by the readiness with which it is removed by hydrolysis. The action of phenylhydrazine hydrochloride on ethyl acetoacetate gives rise to phenylmethylpyrazolone, and also a substance melting at 36° which is identical with that obtained by Nef by the action of acetic chloride on ethyl β-phenylhydrazocrotonate. Ethyl acetoacetate does not yield an acetyl derivative, whilst its analogue, ethyl salicylate, does so readily.

Ethyl sodiosalicylate is prepared by adding either powdered sodium to the toluene solution, or aqueous sodium hydroxide to the ethereal solution of ethyl salicylate; it is a white solid, which is soluble in water with partial decomposition. When bromine is added to an ethereal solution of this substance, a dibromo-substitution product and ethyl salicylate are simultaneously formed, the bromine replacing hydrogen and liberating hydrogen bromide, and the latter then decomposing a further quantity of the substance.

Ethyl dibromosalicylate crystallises from alcohol in nacreous plates, and melts at 100—101°. It is sparingly soluble in hot or cold water, but easily in alkalis. By heating with alcoholic potash, and subsequently treating with dilute sulphuric acid, it is converted into *dibromosalicylic acid*, which crystallises from dilute alcohol in white needles, and melts at 225°. Ethyl dibromosalicylate is reduced to salicylic acid by sodium amalgam in boiling dilute alcoholic solution. When ethyl salicylate is treated with bromine in chloroform solution, *ethyl metabromosalicylate* is formed; it crystallises from alcohol in long needles, and melts at 49—50°. The corresponding acid crystallises from dilute alcohol in colourless needles, melts at 165—166°, and is apparently identical with the metabromosalicylic acid of Hübner and Heinzenberg (*Zeit. Chem.*, 1871, 709).

Ethyl benzoylsalicylate is prepared by treating dry ethyl sodiosalicylate with excess of benzoic chloride. It crystallises from dilute alcohol in small, flaky plates, and melts at 79—80°. It is decomposed into benzoic and salicylic acids by alcoholic potash, showing that the benzoyl radicle is attached to oxygen.

Ethyl diethylsalicylate is formed by treating ethyl sodiosalicylate with ethyl iodide in alcoholic solution. It is a colourless oil which boils at 252°, and yields diethylsalicylic acid on boiling with alcoholic potash. The corresponding methyl compounds agreed with those described by Graebe (*Annalen*, **139**, 137). *Ethyl cuprosalicylate*, prepared by treating alcoholic ethyl sodiosalicylate with copper acetate, like ethyl cupracetoacetate, does not react with alkyl iodides. *Ethyl acetylsalicyate* is prepared by boiling ethyl salicyate with acetic

chloride for some hours in a reflux apparatus. The product is poured into ice-cold water, extracted with ether, the ethereal solution washed with concentrated alkali to separate unchanged ethyl salicyate, and dried over calcium chloride. On evaporating the ether, the acetyl salicylate remains as a thick, colourless oil, which boils at 273°, and is readily decomposed by alcoholic potash.

The products of the action of phenylhydrazine hydrochloride on ethyl acetoacetate are, firstly, phenylmethylpyrazolone, and, secondly, a white, amorphous solid, which melts at 36°, as stated above, and appears to have the composition $C_{12}H_{14}N_2O$. It is soluble in alcohol, chloroform, and ether, but insoluble in cold water and alkalis, and is identical with the oil obtained by Nef (*loc. cit.*) by the action of acetic chloride on ethyl β-phenylhydrazocrotonate, and prepared by the author by the action of acetic chloride on the phenylhydrazine of ethyl acetoacetate. It is not affected by alkalis and concentrated sulphuric acid, and when treated with bromine in chloroform solution, forms a dibromo-additive product, which crystallises in large, colourless prisms, and melts at 111—112°. When treated with methyl iodide, it yields a syrup resembling that obtained in a similar manner from phenylmethylpyrazolone, and is, therefore, probably similar in constitution.

Ethyl acetoacetate is completely decomposed by hydrogen bromide into ethyl bromide, alcohol, ethyl acetate and acetone. If an additive product is formed, which is doubtful, it is very unstable in character.

JN. W.

Ethyl Sodacetoacetate. By A. MICHAEL (*Amer. Chem. J.*, **14**, 481—544; compare Abstr., 1892, 1178 and 1428).—The product of the action of ethyl chlorocarbonate on ethyl sodacetoacetate is not the acid substance ethyl acetomalonate, for which it was mistaken by Conrad and Guthzeit (*Annalen*, **214**, 31), although they could not succeed in displacing any of the hydrogen by sodium, but a neutral substance, which is resolved into ethyl sodacetoacetate and ethyl carbonate by sodium ethoxide, and has, therefore, the constitution COOEt·O·CMe:CH·COOEt (compare Nef, Abstr., 1892, 140). The formation of this compound confirms the view that the sodium in ethyl sodacetoacetate is attached to oxygen and not directly to carbon. There is no reason, however, for attributing a carbinol constitution to ethyl acetoacetate, and its reactions are best explained by means of the ketone formula. The fact that the alkyl and similar groups in the substitution products of ethyl acetoacetate are undoubtedly attached to the methylene carbon, may be explained by assuming the transient existence of an unstable intermediate additive compound, such as ONa·CMeI·CHEt·COOEt, which is formed in consequence of the attraction of the negative iodine of the ethyl iodide for the relatively positive sodoxyl carbon, and of the positive ethyl for the relatively negative methine carbon. As soon, however, as the negative iodine comes within the sphere of influence of the positive sodium, sodium iodide is formed, and the carbon sodoxyl reverts to carbonyl. Nef's hypothesis (*loc. cit.*) that the additive compound is decomposed by the elimination of hydrogen iodide, the hydrogen

of which afterwards replaces the sodium, seems untenable. His contention, too, that acetoacetanilide is an unsaturated substance, because it unites with bromine to form an unstable additive compound, is unsound, since acetic acid itself forms a similar, but much more stable, compound. The formation of the ketonic ethyl acetoacetate from the carbinolic ethyl sodacetoacetate, and *vice versâ*, may be regarded as instances of *merotropy*, or molecular rearrangement due to alteration of stability of the molecule by the introduction or substitution of a foreign atom. When ethyl sodacetoacetate, for instance, is treated with water, it may be assumed that the hydrogen takes the place of the sodium in the first instance, but that the compound so formed, like all other compounds having hydroxyl and hydrogen linked to adjacent unsaturated carbon atoms (hydroxyethylene, for example), is very unstable, and passes at once into the ketonic form by shifting of the hydrogen atom. The hydroxy-compound has thus no separate existence. In the reverse case, when ethyl acetoacetate is acted on by sodium, one of the methylene hydrogen atoms is displaced by the metal, but the compound thus formed at once passes into the carbinol form, owing to the attraction of the negative carbonyl oxygen for the positive sodium. Thus, neither ethyl acetoacetate nor its sodium derivative can be said to have two structures; these, and all other compounds, assume the most stable structure consistent with their composition, and if the composition is altered by the introduction or substitution of foreign atoms, the former structure may be thrown out of balance, and another more stable assumed. All the known phenomena of tautomerism and desmotropy may be explained in terms of this conception of merotropy, in conjunction with the "positive-negative" hypothesis mentioned above.

Ethyl carbethoxyacetoacetate, $COOEt\cdot OCMe{:}CH\cdot COOEt$, is prepared by adding ethyl chlorocarbonate gradually to an ice-cold ethereal suspension of ethyl sodacetoacetate. A small amount, at the most 10 per cent., of ethyl acetomalonate is formed at the same time, and may be dissolved out by dilute aqueous soda. Ethyl carbethoxyacetoacetate boils without decomposition at 136° under 20 mm. pressure (133° under 17 mm.). Its vapour density corresponds with the constitution given above, and not with that of ethyl acetomethanetricarboxylate, as proposed by Nef (*loc. cit.*). It is neutral, moreover, towards alkalis. When dry powdered sodium ethoxide is gradually added to ice-cold ethyl carbethoxyacetoacetate, ethyl carbonate and sodacetoacetate are formed. When an aqueous solution of phenylhydrazine and sodium acetate is added to an alcoholic solution of ethyl carbethoxyacetoacetate (10 grams), phenylmethylpyrazolone and ethyl phenylhydrazine-β-carboxylate, $NHPh\cdot NH\cdot COOEt$, are formed; the latter crystallises in long, white needles, melts at 80—81°, and is sparingly soluble in cold water, moderately soluble in cold, readily in boiling carbon bisulphide, and very soluble in cold alcohol and ether. This reaction tends to confirm the author's view of the constitution of ethyl carbethoxyacetoacetate, as no derivative of ethyl acetoacetate is known in which carboxethyl is detached from carbon by the action of phenylhydrazine. The pyrazolone is probably due to the secondary action of the hydrazine on ethyl

acetoacetate formed during the reaction, as on keeping an alcoholic solution of these two substances for some days, a very good yield of the pyrazolone was obtained (compare Knorr, *Annalen*, **238**, 147).

No definite product was obtained from the action of alcoholic hydroxylamine on ethyl carbethoxyacetoacetate.

Ethyl acetomalonate, $CHAc(COOEt)_2$, is formed, together with the corresponding diaceto-compound, when acetic chloride acts on ethyl sodiomalonate. It is an oily liquid boiling at 120° under 17 mm. pressure, readily soluble in aqueous alkalis, although with partial decomposition, and reprecipitated by acids. The *sodium derivative*, $ONa{\cdot}CMe{:}C(COOEt)_2$, prepared by adding the acetomalonate to an alcoholic solution of sodium ethoxide, crystallises in white, prismatic plates, is very soluble in water, fairly so in alcohol, but only sparingly in ether and concentrated aqueous potash. The presence of ketone carboxyl is proved by the formation of a *hydrazone*, $N_2HPh{:}CMe{\cdot}CH(COOEt)_2$, with phenylhydrazine acetate. This crystallises in white, prismatic plates, melts at 119—121°, and is insoluble in cold water, sparingly soluble in cold alcohol, and easily in hot alcohol.

Ethyl diacetomalonate, $CAc_2(COOEt)_2$, or $OAc{\cdot}CMe{:}C(COOEt)_2$, formed as stated above, boils with slight decomposition at 156°, under 17 mm. pressure, and is neutral in its properties. When it is treated with phenylhydrazine (2 mols.) in ice-cold, ethereal solution, the acetyl is detached with the formation of β-acetylphenylhydrazide (m. p. 127·5—128°).

Conrad and Guthzeit's ethyl methanetricarboxylate (*loc. cit.*), as prepared by these authors' method, and also by the action of ethyl chlorocarbonate on an ethereal suspension of ethyl sodiomalonate, is not a neutral substance, as they state, but dissolves in aqueous alkalis, and forms a *sodium derivative*,

$$C(COOEt)_2{:}C(OEt){\cdot}ONa,$$

when treated with an alcoholic solution of sodium ethoxide. An attempt to methylate ethyl methanetricarboxylate by the Conrad-Limpach method yielded negative results.

The author is unable to confirm his previous statement (Abstr., 1887, 716), as to the absorption of carbonic anhydride by ethyl sodiomalonate.

Ethyl acetylethylmalonate, $CAcEt(COOEt)_2$, is prepared by adding acetic chloride to an ice-cold ethereal suspension of ethyl sodethylmalonate. It is a colourless, neutral oil, which boils with slight decomposition at 137—137·5° under 20 mm. pressure; is sparingly soluble in water, and is miscible with alcohol and ether. It is gradually decomposed by aqueous alkalis, but quickly by sodium ethoxide, ethyl carbonate and sodacetoacetate being formed. With phenylhydrazine acetate, it yields ethyl phenylhydrazine-β-carboxylate.

Ethyl acetomethylmalonate, prepared in a manner similar to that in which the ethyl compound is prepared, boils without decomposition at 131—131·5° (corr.), under 20 mm. pressure, is sparingly soluble in alcohol, and miscible with alcohol and ether. It is neutral towards aqueous alkalis, but is gradually decomposed by them. It is quickly

decomposed by sodium ethoxide into acetic and methyl- and ethyl-malonic acids.

Ethyl carbethoxymethylacetoacetate, COOEt·O·CMe:CMe·COOEt, is prepared in a manner similar to that in which the corresponding ethyl compound is made. It is a colourless oil, which boils at 137° (corr.), under 20 mm. pressure. It is neutral towards aqueous alkalis, but is gradually decomposed by them, and quickly by sodium ethoxide, into ethyl carbonate and methyl acetoacetate. With phenylhydrazine, it behaves like the ethyl compound.

Ethyl propiomalonate forms a *sodium* derivative when treated with sodium ethoxide, and is soluble in aqueous alkalis, and reprecipitated by acids.

Ethyl sodacetosuccinate, prepared in the usual manner from ethyl acetosuccinate, purified by fractionation under 35 mm. pressure (b. p. 167—168°), yields *acetosuccinohydrazanil*,

$$\begin{matrix}\mathrm{COMe{\cdot}CH{\cdot}CO}\\ \mathrm{CH_2{\cdot}CO}\end{matrix}\!\!>\!\mathrm{N{\cdot}NHPh},$$

when treated with phenylhydrazine in ethereal solution. This crystallises in large, white prisms, melts at 175—177°, and is soluble in the usual menstrua. It is dissolved by aqueous alkalis and precipitated unchanged by acetic acid. It forms a *sodium derivative*, $C_{12}H_{11}NaO_3N_2$, which is best prepared, however, by treating ethyl sodacetosuccinate (1 mol.) with free phenylhydrazine (1 mol.) in alcoholic solution, and crystallises in large prisms. It decomposes at 100°, and dissolves in water to a solution, from which it is partly precipitated by acetic acid; a certain amount of Knorr's ethyl acetosuccinate hydrazone (Abstr., 1884, 1380), is, however, formed at the same time. The difference in the behaviour of ethyl acetosuccinate and its sodium derivative towards phenylhydrazine thus points to a difference in constitution, probably of a merotropic character.

The phenylmethylpyrazolone mentioned above may be obtained in almost theoretical quantity by heating a mixture of ethyl acetoacetate and phenylhydrazine hydrochloride or other salt with a little strong hydrochloric or other mineral acid. Analogous results were obtained with the ethyl salts of methyl- and ethyl-acetoacetic and aceto-succinic acids. The hydrazone corresponding with phenylmethyl-pyrazolone is converted quantitatively into that substance, both by acids and by alkalis. Mineral acids do not prevent the formation of the hydrazones of fatty or aromatic aldehydes, as stated by Fischer, although they have a very marked retarding influence in the case of ketones.

Nef's contention that the formation of a hydrazo-derivative by the action of phenylhydrazine on ethyl acetoacetate renders the ketonic formula for the latter impossible, may be answered by the supposition that an intermediate additive compound

$$\mathrm{OH{\cdot}CMe(NH{\cdot}NHPh){\cdot}CH_2{\cdot}COOEt},$$

similar to Collie's compound, $\mathrm{OH{\cdot}CMe(NH_2){\cdot}CH_2{\cdot}COOEt}$ (Abstr., 1885, 373), and to Kuckert's analogous compound with methylamine

and diethylamine (Abstr., 1885, 751), is first formed, and that this is transformed either into the hydrazo-derivative,

$$N_2H_2Ph\cdot CMe{:}CH\cdot COOEt,$$

or under other conditions into the hydrazone,

$$N_2HPh{:}CMe\cdot CH_2\cdot COOEt,$$

with the elimination of water. This author considers this intermediate substance as typical, and would state generally that if a compound HX acts on a carbonyl compound with the elimination of water, an intermediate additive compound $=CX\cdot OH$, is always formed. The elements of water eliminated from such a compound may be derived either from within the molecule, as in the above case, or from several molecules, in which case a condensation product is formed, or the hydroxyl may unite with the hydrogen of a foreign molecule.

The author then replies *seriatim* to many of Nef's statements and criticisms, and concludes by extending the positive-negative hypothesis to the explanation of the laws of addition to unsaturated compounds, and to the demonstration of the absence of necessity for the hypotheses of tautomerism and desmotropy. Jn. W.

Relative Velocity of Lactone Formation in the case of Bibasic γ-Hydroxy-acids. By E. J. Hjelt (*Ber.*, **25**, 3173—3175).—The author has investigated the velocity of lactone formation in the case of the eight acids mentioned below. The method adopted has already been described (Abstr., 1891, 822). The solutions contained 0·00275 molecule (in grams), instead of 0·0055 molecule, and the temperature was 55°. The results are expressed by means of curves. The calculated times required for the conversion of 50 per cent. of the acids into the lactones were as follows:—

Itamalic acid	About	1900	minutes.
Phenylitamalic acid	„	475	„
Methylitamalic „	„	222	„
Isobutylitamalic „	„	110	„
Ethylitamalic „	„	100	„
Hexylitamalic „	„	82	„
Dimethylitamalic acid	„	49	„
Isopropylitamalic „	„	22	„

J. B. T.

Action of Sulphuric acid on β-Trimethylethylidenelactic acid. By T. Schindler (*Monatsh.*, **13**, 647—650).—The author finds that the compound formed by the action of sulphuric acid on β-trimethylethylidenelactic acid at 50°, and stated by Glücksmann to be trimethylacetaldehyde (compare Abstr., 1892, 38), is really methyl isopropyl ketone.

Trimethylethylidenelactic acid is oxidised by chromic acid mixture to trimethylacetic acid, which contains three methyl groups attached to one carbon atom. It therefore appears that sulphuric acid induces

a remarkable molecular rearrangement in the production of the ketone.

The aldehydic properties observed by Glücksmann were, no doubt, due to an admixture of some aldehyde with the ketone.

Attempts to obtain trimethylacetaldehyde by the action of hydrochloric acid on trimethylethylidenelactic acid were without success, the last-named acid remaining unchanged, both in the cold and at the boiling temperature. G. T. M.

Mesitylic acid and Mesitonic acid. By H. Weidel and E. Hoppe (*Monatsh.*, **13**, 603—615; compare Anschütz and Gillet, Abstr., 1888, 1272).—The authors show that mesitylic acid, $C_8H_{13}NO_3$, may be formed by the action of potassium cyanide, not only on the condensation product obtained from acetone and hydrochloric acid, but also on the condensation product of mesityl oxide and hydrochloric acid (compare Pinner, *Ber.*, **15**, 585).

When heated at 160—170° in sealed tubes, with concentrated hydrochloric acid, mesitylic acid loses carbonic oxide, carbonic anhydride, and ammonia, and is converted into mesitonic acid (dimethyllevulinic acid). With hydroxylamine hydrochloride, the latter gives a very characteristic isonitroso-compound, $C_7H_{13}NO_3$, which dissolves in all ordinary solvents, and melts at 94—95°; when heated by itself, it is converted into a lactone-like anhydride. This lactone is formed so readily that it must be supposed that the acid is itself capable of existing in the tautomeric form, $OH\cdot CMe{:}CH\cdot CMe_2\cdot COOH$. G. T. M.

Stereoisomeric Derivatives of the Symmetrical Dimethylglutaric acids. By K. Auwers and H. Kauffmann (*Ber.*, **25**, 3221—3247).—The authors have studied the reactions taking place during the bromination of the above acids. They find that the product obtained by the bromination of dimethylglutaric acid (m. p. 102—103°) depends on the varying conditions of the experiment and the mode of purification of the product, dibromodimethylglutaric acid, dibromodimethylglutaric anhydride (Abstr., 1890, 1098), and two isomeric lactones ($C_7H_9BrO_4$) being formed, according to circumstances. The dibromo-acid is formed if the bromination is carried on at a low temperature and quickly, and the product of reaction, after treatment with ice, separated from the liquefied water as quickly as possible. When the bromination is carried on at a high temperature, the tendency is towards the formation of the anhydride; and if the product of reaction is allowed to remain in contact with the water, the less brominated lactones are produced.

Dibromodimethylglutaric acid, $C_7H_{10}Br_2O_4$, crystallises from benzene in prisms, melts with evolution of gas at 150°, and is soluble in alcohol, ether, water, and ethyl acetate, sparingly so in benzene. When an aqueous solution of this acid is allowed to remain at the ordinary temperature, hydrogen bromide is eliminated, and two isomeric *lactones*, $C_7H_9BrO_4$, of *α-bromo-γ-hydroxydimethylglutaric acid* are formed. One of these, of the probable formula

$$\begin{array}{l} CMeBr \text{———} CO \\ | \qquad\qquad > O, \\ CH_2\cdot CMe(COOH) \end{array}$$

is sparingly soluble in cold water and ether, easily soluble in ethyl acetate, and nearly insoluble in benzene and light petroleum. It crystallises in needles, and melts at 196·5—197°, with blackening and evolution of hydrogen bromide. When the dibromo-acid is treated with *boiling* water, this lactonic acid forms by far the larger portion of the product, only small quantities of the more soluble acid being produced. It is tolerably stable towards water, but, by long-continued boiling with water, is gradually converted into the corresponding hydroxy-lactone $C_7H_{10}O_5$ (m. p. 188°) described by Zelinsky (Abstr., 1892, 436). The same change is readily caused by cold soda solution. The other *bromo-lactone*, $\begin{matrix}CMe(COOH)-\\ CH_2\cdot CMeBr\cdot CO\end{matrix}>O$, is very much more soluble in water than its isomeride. It crystallises in plates or prisms, and melts at 111—113° without decomposition. It is easily soluble in ether, ethyl acetate, and boiling benzene, almost insoluble in light petroleum. Like its isomeride, this lactone is stable towards water, but is converted by soda or by long-continued boiling with water into a dihydroxydimethylglutaric acid melting at 99°. The two bromo-lactones are, like the two dimethylglutaric acids, convertible into one another. When either lactone in benzene solution is heated at 160°, a mixture of the two is produced, but that of higher melting point is always present in the mixture in the larger proportion. When subjected to dry distillation, both acids decompose to a considerable extent, but the distillate always contains much of the lactone of high melting point, and little or none of that of low melting point. It is therefore clear that the lactone melting at 197° is the more stable at high temperatures.

Dibromodimethylglutaric anhydride, obtained by Auwers and Jackson by brominating dimethylglutaric acid (Abstr., 1890, 1098), was obtained by the author by the action of acetic chloride on the dibromo-acid. He finds the melting point to be 94—95°. In moist air, the anhydride is gradually reconverted into the dibromo-acid; with water, it forms the monobromo- and hydroxy-derivatives.

Dihydroxydimethylglutaric acid dihydrazide,

$$CH_2[CMe(OH)\cdot CO\cdot NH\cdot NPhH]_2,$$

was formed by treating the hydroxy-lactone melting at 188° with phenylhydrazine. It crystallises in needles and melts at 176·5°.

A similar *dihydrazide*, crystallising, however, in needles melting at 186°, appears to be formed by the action of phenylhydrazine on the dihydroxy-acid.

The dimethylglutaric acid melting at 127° yielded, on bromination, mixtures of the monobromolactonic acids described above.

The authors also discuss fully the relationships of the isomeric derivatives of the two dimethylglutaric acids, and the probable constitutional explanation of the existence of such isomerides.

L. T. T.

Alkyl Tartrates. By P. Freundler (*Compt. rend.*, **115**, 509—512).—The author has prepared the methyl, ethyl, normal propyl, and isobutyl salts of diacetyltartaric, dipropionyltartaric, and dibutyryltartaric acids, as well as the normal butyl salts of diacetyltartaric

acid, by the action of the respective acid chlorides on the normal tartrates of the various alkyl radicles, and has determined their rotatory power. In the case of ethyl diacetyltartrate, the determination was made on the compound in a state of superfusion. All the salts are somewhat viscous, have very little odour, and can be distilled at the ordinary pressure without appreciable alteration of their rotatory power. This high stability of unsymmetrical compounds is noteworthy.

The specific rotatory powers, $[\alpha]_D$, are given in the following table:—

	Acid.		
Alkyl base.	Diacetyltartaric.	Dipropionyltartaric.	Dibutyryltartaric.
Methyl.....	(−14·29)*	−12·0	−13·0
Ethyl	+ 5·0	+ 0·3	− 1·0
Normal propyl..	+13·5	+ 7·9	+ 5·4
Normal butyl ..	+17·8	—	—
Primary isobutyl	+11·3	+ 9·2	+ 7·1

* Pictet's value.

These results verify the law of the change of sign of the rotatory power. Each compound contains two equal masses (Me·CO·O and COOMe; Et·CO·O and COOEt; and Pr·CO·O and COOPr), and if these two masses were concentrated exactly on the summits of the tetrahedron representing the asymmetrical carbon, the three compounds would remain inactive. The fact that they are optically active confirms Guye's view that although the mass constituting the principal factor allows of the prediction of the sign of optical activity, it is necessary to take into account the arrangement of the atoms.

C. H. B.

Action of Phosphorus Oxychloride on Aromatic Silicates. By H. N. Stokes (*Amer. Chem. J.*, **14**, 545—547).—Phenyl orthosilicate (1 mol.), unlike the aliphatic silicates, does not yield chlorobenzene and silicopyrophosphoryl chloride when heated with phosphorus oxychloride (2 mols.) for 16 hours at 240°, but silicon tetrachloride, phenylphosphoric chloride, $POCl_2·OPh$, and diphenylphosphoric chloride, $POCl(OPh)_2$.

Jn. W.

Preparation of Orthonitrobenzyl Alcohol. By H. G. Söderbaum and O. Widman (*Ber.*, **25**, 3290—3291; compare Paal and Bodewig, this vol., i, 20).—Orthonitrobenzyl alcohol is readily obtained by boiling orthonitrobenzyl chloride (10 grams) with anhydrous potassium carbonate (8 grams) and water (150 c.c.) for four hours in a reflux apparatus; the alcohol separates on cooling, and is purified by recrystallisation from benzene; the yield is 50 per cent. of the chloride employed.

J. B. T.

Benzyl Silicate. By H. N. Stokes (*Amer. Chem. J.*, **14**, 547).—Benzyl alcohol reacts violently with silicon tetrachloride, like an aliphatic alcohol, and not gently, like a phenol. As much as one-fourth of the alcohol is converted into benzyl chloride, and a corresponding amount of the silicon chloride is in consequence converted

into polysilicates. The benzyl silicate which is formed may be separated by distillation, but decomposes on redistillation.

JN. W.

Behaviour of Thiocarbonates towards Phenols. By R. PRIBRAM and C. GLÜCKSMANN (*Monatsh.*, **13**, 623—634).—*Resorcinolcarbothionylic acid* is obtained by heating together at 100° resorcinol and potassium thiocarbonate. It sinters at 150°, melts at 150—155°, gives a red coloration with excess of potash, and, when heated with an excess of alkali hydroxide, yields metadihydroxybenzoic acid, [COOH : $(OH)_2$ = 1 : 2 : 4], as chief product. The bye-product probably consists of 2 : 6-dihydroxybenzoic acid, and there is no indication that any dihydroxyphthalic acid is formed. G. T. M.

Pyrogallol Antimonites. By H. CAUSSE and C. BAYARD (*Compt. rend.*, **115**, 507—509).—100 grams of antimony trichloride is dissolved in 250 c.c. of a solution of sodium chloride saturated at the ordinary temperature, and the filtered liquid is poured in successive small quantities into a solution of 50 grams of pyrogallol in 250 c.c. of the salt solution. A white, flocculent precipitate separates, and, as soon as this ceases to form, no more antimony chloride is added, and the precipitate is left in contact with the liquid for some hours. It gradually becomes much denser, and changes into a mass of small crystals, which is pressed between filter-paper, dried, washed until free from sodium chloride, and again dried at the ordinary temperature. The product is *pyrogallol hydrogen antimonite*, $OH{\cdot}C_6H_3{:}O_2SbOH$. It has the same properties as the corresponding catechol derivative (Abstr., 1892. 1078), and consists of microscopic crystals, insoluble in water, alcohol, benzene, and chloroform, but soluble in nitric, sulphuric, and hydrochloric acids, by the latter of which it is completely decomposed.

The *normal antimonite*, $C_6H_3{:}SbO_3$, is obtained in a similar manner from hot solutions. The pyrogallol solution is heated on a water-bath, and the whole quantity of antimony chloride solution is added. In its general properties, the normal antimonite very closely resembles the hydrogen salt.

Acetic anhydride acts on the normal or hydrogen salt at 100° with production of pyrogallol triacetate. Acetic chloride acts with almost explosive violence, and likewise yields pyrogallol triacetate.

It would seem from these results that the third hydroxyl group in pyrogallol occupies the meta-position, and not the para-position, as is generally assumed. C. H. B.

Metamidodialkylorthotoluidines and their Conversion into Methylene-blue Dyes. By A. BERNTHSEN (*Ber.*, **25**, 3128—3139).—According to Weinberg (Abstr., 1892, 1078), paramidodialkylorthotoluidines do not yield thiosulphonic acids, neither could a thionine dye be obtained. This is not in accordance with the author's views of the formation of the methylene-blue compounds (Abstr., 1889, 775). The author now finds that metamidodimethorthotoluidine [Me : NMe_2 : NH_2 = 1 : 2 : 5] and orthamidodimethylmetatoluidine [Me : NMe_2 : NH_2 = 1 : 3 : 6] yield thiosulphonic acids and methyl-

ene-blue compounds. The amidodimethylorthotoluidine was prepared by methylating nitro-orthotoluidine, purifying the dimethyl compound, and then reducing it.

Metanitrorthotoluidine (60 grams) is heated with methyl iodide (150 grams), sodium hydroxide (35 grams), and methyl alcohol (180 c.c.) in an autoclave for 8—10 hours at the boiling point of a saturated solution of salt. The mixture of mono- and di-methyl compounds is separated either by boiling with acetic anhydride and then distilling the dimethylnitrotoluidine with steam; or by treating the mixture with dilute sulphuric acid (200—250 c.c., sp. gr. = 1·15), when the dimethyl compound only is dissolved.

Metanitromethylorthotoluidine [Me : NHMe : NO_2 = 1 : 2 : 5] is less soluble in alcohol than the dimethyl compound, crystallises in beautiful yellow tablets, and melts at 137°. The *nitrosamine* is obtained as a colourless oil by adding a solution of sodium nitrite to a solution of nitromethyltoluidine in hydrochloric acid. It solidifies after a time and melts at 65°. The *acetyl compound* crystallises from dilute alcohol in pale yellow, rhombohedral crystals, melts at 97°, and is very easily soluble in alcohol.

Metanitrodimethylorthotoluidine [Me : NMe_2 : NO_2 = 1 : 2 : 5] crystallises in small tablets or needles, melts at 47·5°, is very easily soluble in organic solvents, sparingly so in water, and dissolves in dilute hydrochloric and sulphuric acids; from the latter solvents it is precipitated by the addition of water.

Metamidodimethylorthotoluidine is obtained by reduction of the preceding compound with hydrochloric acid and zinc-dust. It boils at 253—254°, is a colourless oil, which soon turns brown on exposure to air; it solidifies when strongly cooled, and melts at 47°. The *sulphate* crystallises in beautiful white needles, and is easily soluble in water, sparingly so in alcohol. A dilute neutral solution of the salt gives with ferric chloride an intense bluish-red coloration, which turns violet on the addition of hydrochloric acid, and, on heating, the odour of quinone is observed. With potassium dichromate, a similar purplish-red is produced. With an alkaline solution of α-naphthol and potassium ferricyanide, it gives the intense blue of the indophenol reaction. With dichromate and dimethylaniline hydrochloride, a deep green indamine is produced. The pure base does not yield a thionine dye when treated with hydrogen sulphide and ferric chloride.

Dimethylparatoluylenediamine hydrogen thiosulphate,

$$NMe_2 \cdot C_6H_3Me(NH_2) \cdot S \cdot SO_3H,$$

is obtained from dimethylparatoluylenediamine in almost theoretical quantities by the method formerly described (*Annalen*, **251**, 50). It crystallises in small, thick prisms, melts at about 240° with decomposition, and is very sparingly soluble in cold water, more easily in hot water and hydrochloric acid. In aqueous solution, it gives colour reactions similar to those of amidodimethylaniline hydrogen thiosulphate. When warmed with soda, it yields the *bisulphide* of amidodimethylorthotoluidine; when reduced with zinc-dust and hydrochloric acid, the *mercaptan*, $NMe_2 \cdot C_6H_2Me(NH_2) \cdot SH$, is obtained. Both these compounds give an easily soluble indamine sulphide with dimethylaniline.

Tetramethylhomoindamine thiosulphate, $C_{17}H_{21}N_3S_2O_3$, is obtained from the above amidodimethylorthotoluidine by converting it into the acid thiosulphate, and, after a few minutes, adding an aqueous solution of dimethylaniline hydrochloride and the calculated quantity of chromate. The product is obtained in slender, green needles, and is purified by washing with dilute acetic acid. It crystallises with 1 mol. H_2O, which it loses at 90—95°.

Homomethylene-blue, $C_{17}H_{20}N_3SCl$, is obtained from the preceding compound in the manner formerly described for methylene-blue, which it closely resembles. The *hydriodide* crystallises with 1 mol. H_2O in small needles, and is very sparingly soluble in water.

The mono- and di-ethyl derivatives of metanitro-orthotoluidine are obtained in a similar way to the methyl derivatives. The mixed product is purified by crystallising the free bases from a small quantity of alcohol, in which the monethyl derivative is less soluble. The diethyl compound is then purified in the same way as described for the dimethyl compound by means of acetic anhydride.

Nitroethylorthotoluidine crystallises from alcohol in large, dark yellow plates, and melts at 98°. The *acetyl compound* crystallises from dilute alcohol in colourless tablets or prisms, and melts at 96—97°.

Metanitrodiethylorthotoluidine is obtained as a yellow oil by distillation with steam and is sparingly soluble in water, easily so in dilute hydrochloric or sulphuric acid.

Metamidodiethylorthotoluidine is a colourless oil which quickly darkens on exposure to air, and boils at 266—267°. The *sulphate*, $C_{11}H_{18}N_2H_2SO_4$, crystallises in large, colourless tablets. The dilute aqueous solution of the salt gradually develops a purple-red coloration when mixed with ferric chloride, and with dichromate, a red coloration. With α-naphthol and potassium ferricyanide, it gives a violet-red, with dimethylaniline hydrochloride and dichromate, a dirty, reddish-brown precipitate.

Amidodiethylorthotoluidine hydrogen thiosulphate is not obtained so readily as the dimethyl compound. It crystallises in small, colourless prisms, and melts at 210—215°. With soda, it yields a bisulphide; with zinc and hydrochloric acid, a mercaptan; both these compounds give indamines. It gives a blue dye, having the characteristic properties of the thionine dyes. E. C. R.

Metamidodialkylorthotoluidines and their Conversion into Methylene-blue Dyes. By A. Bernthsen (*Ber.*, **25**, 3366—3368; compare preceding abstract).—The author has previously shown that the metamidodiethylorthotoluidine, $C_6H_3Me(NEt_2)\cdot NH_2$, [1 : 2 : 5], prepared by ethylating the nitrotoluidine [Me : NH_2 : NO_2 = 1 : 2 : 5] and reducing the resulting product, when oxidised with chromate, in the presence of a thiosulphate, yields amidodiethylorthotoluidine hydrogen thiosulphate, $NEt_2\cdot C_6H_2Me(NH_2)\cdot S\cdot SO_3H$. Weinberg (Abstr., 1892, 1078) was unable to effect this conversion, but he prepared his base from metamidoethylorthotoluidine by acetylating, ethylating, and eliminating the acetyl group. It is now shown that this method gives an impure product, but the pure base

can be isolated from it, and then yields the thiosulphate mentioned above. C. F. B.

Conversion of Tanacetoxime into 1 : 3 : 4-Cymidine. By F. W. Semmler (*Ber.*, **25**, 3352—3354).—If an alcoholic solution of tanacetoxime (this vol., i, 107) is boiled and a mixture of dilute sulphuric acid and alcohol gradually added, a portion of the oxime is converted into the hitherto unknown *cymidine*, $C_6H_3Pr^{\beta}Me{\cdot}NH_2$ [$Pr^{\beta} : NH_2 : Me = 1 : 3 : 4$], which was identified by converting it, by the diazo-reaction, into 1 : 3 : 4-carvacrol. It is a basic substance which boils at 118—121° under 13 mm. pressure, and has a sp. gr. of 0·9442 at 20°, and refraction $[n]_D = 1{\cdot}5387$. Its odour resembles that of aniline, and at the same time that of thymol; it forms a sparingly soluble sulphate, its hydrochloride colours a deal splinter yellow, and it gives a red coloration with bleaching powder. When its platinochloride is heated with excess of platinic chloride, the solution turns green, then violet-blue, and finally red, and yields a deep blue, or a red, colouring matter when extracted with ether. C. F. B.

Condensation Products of Amidophenols and Amidophenyl Ethers with Aldehydes and Ketones. By C. Philipp (*Ber.*, **25**, 3247—3249).—The author obtained benzylideneparamidophenol by the action of benzaldehyde on a hot aqueous solution of paramidophenol hydrochloride and sodium acetate, and also by the admixture of alcoholic solutions of the phenol and aldehyde. He finds the melting points to be 181°; Haegele (Abstr., 1892, 1451) gave it as 163°. It combines with mineral and organic acids to form very stable additive products, crystallising in yellow needles. The etheric derivatives are obtained by direct substitution or by condensation of phenol ethers.

Benzylideneparamidomethoxybenzene, $CHPh{:}N{\cdot}C_6H_4{\cdot}OMe$, forms colourless scales melting at 62°. The *ethoxy*-derivative forms colourless scales melting at 76°. L. T. T.

Acidoxyl Derivatives of Diphenylethylenediamine and Ditolylethylenediamine. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **25**, 3253—3262).—The following compounds, containing nitrogen atoms combined with three different radicles, described in this and the next abstract, and on p. 98, were prepared in order to determine if they exist in stereometric modifications. In no case was a stereometric isomeride obtained.

Dimonochloracetyldiphenylethylenediamine, $C_2H_4(NPh{\cdot}CO{\cdot}CH_2Cl)_2$, is obtained, together with diphenylethylenediamine hydrochloride, by the action of chloracetic chloride on diphenylethylenediamine dissolved in ether. It crystallises in colourless, oblique prisms, and melts at 153—154°.

Dimonobromacetyldiphenylethylenediamine, obtained in a similar way to the preceding compound, crystallises in large prisms, and melts at 136°.

Dimonobromopropionyldiphenylethylenediamine is obtained together with diphenylethylenediamine hydrobromide by the action of bromo-

propionic bromide on diphenylethylenediamine dissolved in benzene. It is separated from the above hydrobromide by extracting the product with benzene, in which the latter is insoluble. It crystallises in small, dull tablets, and melts at 184°.

Di-α-monobromonormalbutyryldiphenylethylenediamine crystallises in transparent tablets, and melts at 98°.

Di-α-monobromisobutyryldiphenylethylenediamine crystallises in white, uncharacteristic crystals, and melts at 143°.

Diacetyldiorthotolylethylenediamine, $C_2H_4(NAc{\cdot}C_7H_7)_2$, is obtained in theoretical quantity by adding acetic anhydride to orthoditolylethylenediamine. It crystallises in colourless prisms, and melts at 152—153°.

Dimonobromacetyldiorthotolylethylenediamine crystallises in colourless needles, and melts at 205°.

Dimonobromopropionyldiorthotolylethylenediamine is obtained as a white, viscous mass which, on extraction with benzene, yields a product melting at 139—180°. By crystallisation from ether, it is obtained in oblique prisms, melting at 181°. To determine if a lower-melting isomeride is present in the crude product, a quantitative experiment was made. The theoretical yield of the acidoxyl compound was obtained melting between 176° and 181°, together with diorthotolylethylenediamine hydrobromide in molecular proportion.

Di-α-bromonormalbutyryldiorthotolylethylenediamine crystallises with 1 mol. of benzene, and melts at 190°.

Di-α-bromisobutyryldiorthotolylethylenediamine is obtained, together with monobromisobutyryldiorthotolylethylenediamine melting at 135—137°, in a similar way to the preceding compounds. It crystallises in colourless, rhombohedral tablets, and melts at 172—173°.

Diacetyldiparatolylethylenediamine crystallises in colourless, rhombohedral prisms and melts at 137—139°.

Dimonobromacetyldiparatolylethylenediamine crystallises in colourless, transparent parallelopipeds, and melts at 196°.

Di-α-bromopropionyldiparatolylethylenediamine melts at 182°, and otherwise resembles the preceding compound.

Di-α-bromonormalbutyryldiparatolylethylenediamine melts at 125°, has similar properties to the preceding compound, but is more easily soluble in ether and light petroleum.

Di-α-monobromisobutyryldiparatolylethylenediamine crystallises in colourless, long, six-sided prisms, melts at 175°, and has the same solubility as the preceding compound, but is more sparingly soluble in ether and light petroleum.

The solubilities of these compounds in the ordinary solvents are described at length. E. C. R.

Derivatives of Propylenediamine and Pseudobutylenediamine. By C. Trapesonzjanz (*Ber.*, **25**, 3271—3282).—*Diphenylpropylenediamine*, $NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}NHPh$, is obtained by the action of propylene bromide on aniline. It is a very viscid, colourless oil, and boils at 265° under 60 mm. pressure. The *hydrochloride* crystallises in spherical aggregates, turns red on exposure to air, and melts at

100° with evolution of gas. The *platinochloride* is obtained as a yellow precipitate. The *diacetyl* compound forms irregular crystals, and melts at 146—147°. The *dibenzoyl* derivative crystallises in long, white tablets, and melts at 136—137°.

Propylenediphenylcarbamide, $CO<^{NPh\cdot CHMe}_{NPh\cdot CH_2}$, is obtained by adding carbonyl chloride to diphenylpropylenediamine both dissolved in benzene. It melts at 121—122°, is easily soluble in hot alcohol, benzene, chloroform, and carbon bisulphide, and insoluble in water; it dissolves in concentrated sulphuric acid, from which it is precipitated by adding water, and is not attacked by boiling aqueous potash.

Methyldiphenylpiperazine, $NPh<^{CHMe\cdot CH_2}_{CH_2-CH_2}>NPh$, is obtained by heating diphenylpropylenediamine with ethylene bromide and anhydrous soda at 150°. It crystallises in small, white prisms, melts at 100°, and is easily soluble in benzene, chloroform, carbon bisulphide, hot alcohol, and ether, less so in light petroleum, insoluble in water, and dissolves in warm concentrated sulphuric acid. It cannot be prepared by heating propylene bromide with diphenylethylenediamine and soda at 160°. The influence of the methyl group in propylene bromide is also seen by the fact that in the preparation of diphenylethylenediamine, larger or smaller quantities of the tertiar base (diphenylpiperazine) are always formed, whereas in the preparation of the corresponding propylene base, only the secondary base is formed. Also the bases obtained by the action of aniline and toluidine on propylene bromide are oily liquids, whereas those obtained from ethylene are all solid compounds. The author explains this influence of the methyl group by Bischoff's hypothesis (Abstr., 1891, 892).

Diphenyldimethylpiperazine, $NPh<^{CHMe\cdot CH_2}_{CH_2\cdot CHMe}>NPh$ or

$$NPh<^{CH_2\cdot CHMe}_{CH_2\cdot CHMe}>NPh,$$

is obtained by heating diphenylpropylenediamine with propylene bromide at 140—150° for five hours. A viscid colourless oil is obtained which boils at 250—270° under 50 mm. pressure, and is contaminated with diphenylpropylenediamine, which the author was unable to eliminate.

Diorthotolylpropylenediamine, $C_7H_7\cdot NH\cdot CHMe\cdot CH_2\cdot NH\cdot C_7H_7$, is obtained by heating orthotoluidine with propylene bromide in a reflux apparatus at 150—160°. It boils at 250—265° under a pressure of 70 mm., and at 280° under 120 mm. The *diacetyl* derivative crystallises in small, oblong tablets, and melts at 101—102°.

Propylenediorthotolylcarbamide, $CO<^{N(C_7H_7)\cdot CHMe}_{N(C_7H_7)\cdot CH_2}$, obtained by the action of carbonyl chloride on the above diamine, crystallises from dilute alcohol in small, irregular prisms, melts at 93°, and is soluble in the ordinary solvents with the exception of light petroleum.

Diparatolylpropylenediamine, obtained in a similar way to the ortho-compound, is a pale-yellow oil, and boils at 276—278° under 48 mm. pressure. The *diacetyl* compound crystallises from alcohol and ether in small, white prisms, and melts at 113·5—114°. The *dibenzoyl* compound melts at 151—152°.

Propylenediparatolylcarbamide crystallises in small, colourless prisms, melts at 129·9°, and is easily soluble in benzene, chloroform, alcohol, and carbon bisulphide, less so in ether, and insoluble in light petroleum.

Diparatolylmethylpiperazine is obtained by heating diparatolylpropylenediamine with ethylene bromide and anhydrous soda for one hour at 150°. It crystallises from alcohol in small, white needles, melts at 105°, and is easily soluble in most solvents, less so in light petroleum.

Di-α-naphthylpropylenediamine is obtained by heating a mixture of α-naphthylamine, propylene bromide, and dry sodium carbonate at 165° for 1—1½ hours. It crystallises in small, white aggregates, and melts at 218—220°.

Di-β-naphthylpropylenediamine is obtained, together with dinaphthylamine, by heating a mixture of β-naphthylamine and propylene bromide at 170—180°. The formation of dinaphthylamine may be prevented by adding dry soda to the mixture. The *hydrochlorids* crystallises in small aggregates, and melts at 190—191°.

Propylenedi-β-naphthylcarbamide crystallises in slender needles, melts at 157°, and is easily soluble in benzene, chloroform, hot acetone, and acetic acid.

Diphenyldimethylethylenediamine, NHPh·CHMe·CHMe·NHPh, is obtained by heating a mixture of aniline and pseudobutylene bromide at 160° for four hours. It is a pale-yellow oil, and boils at 225—228° under 41 mm. pressure. The *hydrochloride*, $C_{16}H_{22}N_2Cl_2$, crystallises in short needles, melts at 205°, and decomposes at 230°. The *diacetyl derivative* crystallises in small, prismatic tablets, and melts at 195—196°. The *dibenzoyl derivative* is precipitated from chloroform by absolute ether in small, crystalline aggregates, and melts at 243—244°.

Dimethylethylenediphenylcarbamide, $CO<\begin{matrix}NPh\cdot CHMe\\ |\\ NPh\cdot CHMe\end{matrix}$, crystallises in white prisms, melts at 139—141°, and is easily soluble in most solvents, sparingly so in petroleum, and insoluble in water.

E. C. R.

Decomposition of Diazo-compounds. By J. Hausser and P. T. Muller (*Compt. rend.*, **114**, 1438—1441).—The decomposition of diazo-compounds by water, as the authors have already shown (Abstr., 1892, 768), does not in all cases follow the ordinary laws of mass action. To the substances formerly mentioned as abnormal in their behaviour must now be added diazobenzene sulphate, in the decomposition of which a retardation occurs similar to that previously noted in the other instances. The authors show that the explanation which they have already given of this retardation is correct, and that

it is due to the influence of the phenol liberated during the reaction. As Hirsch has shown, phenol does react with diazobenzene salts (Abstr., 1891, 437), and an action in the sense of the equation

$$C_6H_5\cdot N_2\cdot SO_4H + C_6H_5\cdot OH = C_6H_5\cdot N_2\cdot OC_6H_5 + H_2SO_4$$

may, perhaps, take place. Other derivatives, however, exercise a retarding influence on the above reaction, whereas open-chain compounds such as alcohol, oxalic acid, and sugar are without effect. The influence must, therefore, in some manner depend on the benzene nucleus. H. C.

Action of Diazobenzene on Malonic acid. By H. v. Pechmann (*Ber.*, **25**, 3175—3190).—It is already known that the compound obtained by the action of malonic acid on diazobenzene is identical with that formed from mesoxalic acid and phenylhydrazine; on treating ethyl mesoxalate hydrazone with acetic anhydride, carbonic anhydride is evolved and *ethyl glyoxylate acetylhydrazone*, NPhAc·N:CH·COOEt, is formed; it crystallises from alcohol, melts at 95°, and, on hydrolysis, yields glyoxylic acid hydrazone; the correctness of the hydrazone formula for the original compound is thus finally proved.

By the action of ethyl mesoxalate hydrazone on diazobenzene chloride in molecular proportion at low temperatures, a compound is obtained which has the formula NPh:N·C(N·NHPh)·COOEt, and crystallises from alcohol in lustrous, brownish-yellow plates; these when allowed to remain in contact with the mother liquor change into red prisms with a blue fluorescence; both forms melt at 117·5° when quickly heated; the compound is also formed from ethyl sodiomalonate and anhydrous diazobenzene chloride in alcoholic solution, and from diazobenzene and ethyl benzeneazoacetoacetate, or directly from ethyl acetoacetate (compare Bamberger, Abstr., 1892, 162). The author suggests the name *ethyl formazylcarboxylate* for the compound, the group NPh:N·C:N·NHPh being termed *formazyl*. The yield is almost quantitative. The *acetyl derivative* is formed by heating the substance with zinc chloride and acetic anhydride; it crystallises in yellow needles. *Methyl formazylcarboxylate*,

$$NPh{:}N\cdot C(N\cdot NHPh)\cdot COOMe,$$

is prepared by dissolving ethyl malonate (1 mol.) in sodium methoxide (1 mol.) solution, and adding it gradually to diazobenzene chloride (1 mol.) in methyl alcoholic solution, the temperature not being allowed to exceed 0°; it crystallises from methyl alcohol in red needles melting at 134—135°, and, on hydrolysis, yields the same acid as the ethyl salt; molecular weight determinations agree with the above formula. The yield is equal to about half the ethyl malonate employed. *Methyl mesoxalate hydrazone*, which crystallises in yellow needles melting at 129°, also yields methyl formazylcarboxylate on treatment with diazobenzene chloride.

Formazylcarboxylic acid, NPh:N·C(N·NHPh)·COOH, is prepared by dissolving either the ethyl or methyl salt in 10 parts of alcohol,

and boiling the solution for five minutes with 5 parts of soda (12 per cent.); the precipitated acid is purified by solution in potash and crystallisation from dilute alcohol; it is deposited in small, red needles, melts at 162—163° with decomposition, and is readily soluble in benzene or chloroform, but sparingly so in alcohol and ether. The salts are sparingly soluble and red or brown in colour; the *potassium salt* crystallises in small, lustrous plates; the *silver salt* is violet coloured, and, on treatment with methyl iodide or ethyl iodide, yields the methyl and ethyl salts previously described.

Formazyl hydride, NPh:N·CH:N·NHPh, may be obtained in three ways: (1) By heating formazylcarboxylic acid, carbonic anhydride being evolved. (2) By heating phenylhydrazine (3 parts) with ethyl formate (1 part) and alcohol (8 parts) for 24 hours in a reflux apparatus; this is the best method of preparing formylphenylhydrazine (m. p. 145°); the yield of hydrogen formazyl is 40 per cent. of the ethyl formate employed. (3) Malonic acid (26 grams), and sodium acetate (50 grams) are dissolved in ice-cold water (400 grams) and quickly mixed with half the theoretical quantity (1 mol.) of diazobenzene chloride solution, prepared from aniline (23 grams), hydrochloric acid, sp. gr. 1·19 (57 grams), sodium nitrite (18 grams), and sodium acetate (50 grams); the mixture is allowed to remain for 12—15 hours at 0°, the deposited product is separated, washed, dried, and dissolved in methyl alcohol, the solution, after being freed from resinous matter by the cautious addition of water, is diluted, and the product purified by repeated crystallisation from methyl alcohol. The yield is equal to the malonic acid employed. Formazyl hydride is deposited in small, red needles which exhibit a violet lustre, and melt at 116—119° with previous softening at 100°. The *acetyl derivative* is prepared by heating formazyl hydride with 4 parts of acetic anhydride, to which zinc chloride has been added, but it may be obtained more readily from the carboxylic acid; it crystallises from alcohol or acetone in orange-yellow needles melting at 188—189°, and gives a blue coloration with sulphuric acid.

By the action of zinc dust (0·5 part) and acetic anhydride (3—4 parts) on formazyl hydride, or on its acetyl derivative, the *diacetyl derivative* of a reduction compound, $N_2HPhAc{\cdot}CH{:}N{\cdot}NAcPh$, is obtained; it crystallises from alcohol, in which it is sparingly soluble, in small, rhombic plates, melts at 197°, and gives a red coloration with alkalis, and a pale-yellow with ferric chloride. In the preparation of the preceding compound, a *monacetyl derivative*, $N_2HPhAc{\cdot}CH{:}N{\cdot}NHPh$, is also formed; this crystallises in needles, melts at 163—164°, gives no coloration with ferric chloride, and is readily converted into the above diacetyl derivative.

Formazylazobenzene, $NHPh{\cdot}N{:}C(N{:}NPh)_2$, is formed by the action of diazobenzene chloride on formazylcarboxylic acid or mesoxalic acid hydrazone in alkaline solution; it is, however, most readily prepared from diazobenzene chloride (3 mols.) and malonic acid (1 mol.) in presence of sodium acetate. The product is purified by repeated crystallisation from alcohol, and is deposited in dark-red, bronze, lustrous plates melting at 162—163°; it is readily soluble in chloroform, acetone, or benzene, and gives a blue coloration with sulphuric

acid, changing to red on the addition of water; with reducing agents, a colourless compound is formed. J. B. T.

Mixed Azo-compounds. By H. v. PECHMANN (*Ber.* **25**, 3190—3200).—The compound prepared by Pechmann and Jenisch (compare Abstr., 1892, 161) from acetonedicarboxylic acid and diazobenzene proves to be *mesoxalic dihydrazone*, $CO(CH{:}N{\cdot}NHPh)_2$, not dibenzeneazoacetone, $CO(CH_2{\cdot}N{:}NPh)_2$, since, on heating with acetic anhydride and zinc chloride, it yields a *diacetyl derivative*, $CO(CH{:}N{\cdot}NAcPh)_2$, which crystallises in yellow needles, melts at 167—168°, and yields acetanilide. The compound, believed by Bamberger to be the symmetrical hydrazone of mesoxalic aldehyde (Abstr., 1892, 162), proves to be *formazyl methyl ketone*,

$$NPh{:}N{\cdot}C{:}N{\cdot}NHPh{\cdot}Ac$$

(compare next abstract). It would appear from the above, as well as from the researches of Japp and Klingemann, that all compounds formed from diazobenzene and 1 : 3-diketo-derivatives must be hydrazines. Beyer and Claisen showed that benzeneazoacetylacetone (from acetylacetone and diazobenzene) has the formula $CHAc_2{\cdot}N_2Ph$, since it yields a hydrazone which is readily converted into a pyrazole derivative. By the introduction of an acid radicle into the molecule of benzeneazoacetylacetone and subsequent decomposition of the product, acid anilides are obtained, showing that one of the hydrogen atoms of the original compound must be linked to nitrogen; the compound is probably tautomeric, since, in some respects, it behaves as an azo-derivative; but in the free state it appears to be represented by the hydrazine formula, as it reacts with sulphuric acid and potassium dichromate.

The *benzoyl derivative* of "benzeneazoacetylacetone,"

$$CAc_2{:}N{\cdot}NBzPh,$$

is prepared from the sodium salt by benzoic chloride; it crystallises from alcohol in lustrous, rhombic plates, melts at 160—161°, and gives a brown coloration with sulphuric acid and potassium dichromate. On treatment with stannous chloride and hydrochloric acid, benzanilide is formed.

The *acetyl derivative*, $CAc_2{:}N{\cdot}NPhAc$, is prepared from the hydrazone by the action of acetic anhydride and zinc chloride; it crystallises from dilute alcohol in lustrous, rectangular plates, melts at 145—146°, and yields acetanilide.

The author then proceeds to show at length, by means of formulæ, how hydrazine derivatives may be formed when diazobenzene acts on various substances; he suggests that the process is analogous to the aldol condensation, and, excluding a few cases where experimental evidence is wanting, concludes that the compounds of diazobenzene with aliphatic derivatives are hydrazines. J. B. T.

Action of Diazobenzene on Ethyl Acetoacetate. By E. BAMBERGER and E. WHEELWRIGHT (*Ber.*, **25**, 3201—3213; compare v. Pechmann, preceding abstracts).—Ethyl formazylcarboxylate,

NPh:NC:N·NHPh·COOEt, has been prepared, independently of the authors, by the action of ethyl acetoacetate (1 mol.) on diazobenzene (2 mols.); the *silver salt*, NPh:N·C(N·NAgPh)·COOEt, is brownish-red. *Sodium formazylcarboxylate* crystallises in small, lustrous, dark red needles, and melts at 200—201° with evolution of gas; the *ammonium salt* is also crystalline, and readily soluble; the *barium*, *calcium*, *zinc*, *lead*, and *copper salts* have been prepared; they are all dark red, and sparingly soluble.

Formazylhydrazide has already been described (*loc. cit.*); it may also be obtained by heating the acid for a considerable time with alcoholic potash.

Formazylazobenzene (phenylazoformazyl), $C(NPh:N)_2:N\cdot NHPh$, crystallises in needles and also in dark red, lustrous plates; its formation from diazobenzene and pyruvaldehydephenylhydrazone has already been described (Abstr., 1892, 162); it is, however, obtained by the action of diazobenzene on acetone, acetaldehyde, and pyruvic acid, all of which contain a methyl group linked to the carbonyl group. By the action of mineral acids on the ethereal salts of formazylcarboxylic acid, aniline and phenazine are formed, together with a third compound, which crystallises in orange-red, lustrous needles, and melts at 74—75°; it has the formula $C_7H_5N_3$, and is probably identical with α-phentriazine.

The authors suggest that in the formazyl group the position of different radicles should be indicated by the prefix *a* or *h*, according to whether the radicle be linked to the "azo-" or to the hydrazine group; they consider that the action of diazobenzene on aldehydes or ketones (in strongly alkaline solution) proceeds according to one or more of the following three typical equations:—

1. $R_1\cdot CO\cdot CH_2\cdot R + N_2Ph\cdot OH = R_1\cdot CO\cdot CR:N\cdot NHPh + H_2O.$
2. $R\cdot CO\cdot CH_3 + 2N_2PhOH = R\cdot CO\cdot C(N_2Ph):N_2HPh + 2H_2O.$
3. $R\cdot CO\cdot CR_1:N\cdot NHPh + N_2PhOH = N_2Ph\cdot CR_1:N_2HPh + R\cdot COOH.$

Their views regarding the constitution of methyl formazyl ketone are in agreement with those of v. Pechmann (preceding abstracts).

J. B. T.

Phenylhydrazidoisobutyronitrile and the Products of its Hydrolysis. By F. Eckstein (*Ber.*, **25**, 3319—3326).—The author has prepared phenylhydrazidoisobutyronitrile by adding the calculated quantity of acetone to an ethereal solution of phenylhydrazine and hydrogen cyanide, cooled to 0°, and subsequently heating the mixture for two hours on the water-bath in a closed vessel. He has also prepared the nitrile by Reissert's method (Abstr., 1884, 1152), and finds that the products are in both cases identical. From the first mode of formation, it therefore follows, in opposition to Reissert's views, that the nitrile has the symmetrical formula $NHPh\cdot NH\cdot CMe_2\cdot CN$. When the nitrile is dissolved in absolute alcohol, and the solution saturated with hydrogen chloride as directed by Reissert (*loc. cit.*), the *amide*, $C_9H_{13}N_2\cdot CONH_2$, is obtained, a compound crystallising from benzene as a white, silky powder and melting at 117°. Reissert be-

lieved the last-named compound to be an imido-derivative. The author also finds that, contrary to Reissert's statement, phenylhydr. azidoisobutyronitrile is converted into the amide just described, when it is allowed to remain in the cold with concentrated hydrochloric acid (10 parts) for 10—12 days; when the amide is boiled for a protracted period with concentrated hydrochloric acid (10 parts), it is quantitatively converted into phenylhydrazidoisobutyric acid (m. p. 165—166°), the *hydrochloride* of which crystallises from ether in four-sided, truncated pyramids, and melts at 182°. When phenylhydr. azidoisobutyramide (Reissert's imide) is treated with tin and hydrochloric acid, ammonia is one of the products, as stated by Reissert; but the case is simply one of hydrolysis, and not of reduction, as phenylhydrazidoisobutyric acid is the other product. Phenylhydrazidoisobutyric acid is only partially attacked by tin and hydrochloric acid, aniline being identified as one of the products; but anilidobutyric acid was not recognised; the author therefore considers it desirable that Reissert should re-examine the products of this reaction. When phenylhydrazidoisobutyric acid is boiled with sodium hydroxide and animal charcoal, an acid, melting at 132°, is obtained; it is under investigation. A. R. L.

Condensation of β-Benzoylphenylhydrazine with Aldehydes. By G. Minunni (*Gazzetta*, **22**, ii, 230—244).—β-Benzoylphenylhydrazine and pure benzaldehyde do not react at 200°, but with a certain sample of benzaldehyde containing some unknown impurity, reaction occurred readily at 125—130°. The mass first liquefies, and in 4—5 hours resolidifies; it is extracted on the water-bath with a little alcohol, and the residue dissolved in much hot alcohol. After filtration and concentration, a substance of the composition $C_{33}H_{28}N_4O_2$ is obtained in white flocks which melt at 218—219°; it probably contains two benzoyl groups. It is sparingly soluble in alcohol, ether, chloroform, and benzene, and readily soluble with partial decomposition in sulphuric acid, hydrochloric acid, or warm glacial acetic acid; in the first case benzoic acid is formed. With alcoholic potash, it yields a crystalline substance melting at 90—92°, which is still under examination.

β-Benzoylphenylhydrazine and pure benzaldehyde react readily in presence of anhydrous oxalic acid, but the condensation product described above could not be isolated from the mass; on heating a mixture of benzoylphenylhydrazine (5 grams), benzaldehyde (4 grams), and zinc chloride (2·5 grams) at 160—170°, the compound of the composition $C_{33}H_{28}N_4O_2$ is produced. The crystalline *diacetyl* derivative, $C_{33}H_{26}N_4O_2Ac_2$, melts at 257°. A *tetrabenzoyl* compound, of the formula $C_{33}H_{26}N_4O_2Bz_2 = C_{19}H_{16}N_4Bz_4$, was obtained; it forms white flocks, and melts at 168—169°. By the action of sodium nitrite and hydrochloric acid on the alcoholic solution of the condensation product, an oil is produced which readily decomposes with evolution of nitrous fumes, and, on treatment with potash, yields a substance which crystallises in needles and melts at 91—92°.

β-Benzoylphenylhydrazine and salicylaldehyde yield a crystalline product melting at 174°. The author is continuing the investigation. W. J. P.

Action of Phenylhydrazine on some Isomeric Aldoximes. By G. Minunni and G. Corselli (*Gazzetta*, **22**, ii, 139—149).—Minunni and Caberti (Abstr., 1891, 1361) have shown that α- and β-benzaldoxime and benzaldehyde give an α-hydrazone with phenylhydrazine: the authors now show that the normal hydrazone is always obtained with other α- and β-aldoximes. They consider that Hantzsch's investigations of the acetyl derivatives of the aldoximes (Abstr., 1891, 443) support Minunni's views of their constitutions (Abstr., 1891, 1354).

On heating α-paranisaldoxime, $OMe{\cdot}C_6H_4{\cdot}CH{:}NOH$ (5·5 grams), with phenylhydrazine (4 grams) on the water-bath for five hours, ammonia is evolved, and, on cooling, the hydrazone is obtained as a crystalline mass. The same product is formed on heating β-paranisaldoxime, $OMe{\cdot}C_6H_4{<}\begin{matrix}N{\cdot}OH\\ \|\\ CH\end{matrix}$, with phenylhydrazine in molecular proportion on the water-bath.

α-Metanitrobenzaldoxime melts at 122° (not at 118—119°), and gives an almost quantitative yield of the normal hydrazone on heating with phenylhydrazine. It separates from boiling alcohol in acicular red crystals melting at 123°. The same hydrazone is obtained on heating a concentrated alcoholic solution of metanitrobenzaldehyde and phenylhydrazine in molecular proportion, or by heating β-metanitrobenzaldoxime and phenylhydrazine together.

α- or β-Cuminaldoxime, when similarly heated with phenylhydrazine, yields the normal *hydrazone*, which crystallises from alcohol in long, colourless needles, and melts at 124—125°. The same substance is formed, with development of heat, on mixing concentrated alcoholic solutions of cuminol and phenylhydrazine. W. J. P.

New Method of determining the Structure of the Oximido-group in Ethers of the Oximes. By G. Minunni and G. Corselli (*Gazzetta*, **22**, ii, 149—164).—On treating the ether of an α-aldoxime with phenylhydrazine, a hydrazone and an α-substituted hydroxylamine are obtained, $R{\cdot}CH{:}NOR + NH_2{\cdot}NHPh = R{\cdot}CH{:}N{\cdot}NHPh + NH_2{\cdot}OR$. With the ethers of the β-oximes, a β-substituted hydroxylamine is formed, $R{\cdot}CH{<}\begin{matrix}NR\\ |\\ O\end{matrix} + NH_2{\cdot}NHPh = R{\cdot}CH{:}N{\cdot}NHPh + R{\cdot}NH{\cdot}OH$. These reactions afford a means of discriminating between α- and β-aldoximes.

α-Benzaldoxime benzyl ether cannot be obtained free from benzyl chloride by Beckmann's method (Abstr., 1889, 607). In order to prepare a pure substance, a large excess of the sodium derivative of the oxime must remain in contact with benzyl chloride for many days; the benzyl ether is then precipitated with water and extracted with ether. On heating α-benzaldoxime benzyl ether with phenylhydrazine in molecular proportion, a product is obtained which partly solidifies on cooling; after filtration, the oily filtrate is repeatedly heated, cooled, and filtered until no further separation of crystals occurs on cooling. The crystalline substance is the hydrazone of benzaldehyde, and melts at 156—157°; on distilling the oil in a

current of steam, extracting the distillate with ether, and passing dry hydrogen chloride into the ethereal solution, crystalline laminæ of α-benzylhydroxylamine hydrochloride are precipitated.

On heating a mixture of α-benzaldoxime methyl ether and phenylhydrazine in molecular proportion at 160—165°, in an oil-bath, the mass solidifies on cooling. The gaseous products are absorbed by hydrochloric acid; on evaporating this solution to dryness, dissolving the residue in alcohol, and adding ether, α-methylhydroxylamine hydrochloride melting at 146—147° separates. The solid product of the reaction, when washed with ether and crystallised from alcohol, is found to be benzaldehyde hydrazone; the ethereal washings contain small quantities of the unaltered methyl ether and phenylhydrazine.

α-Anisaldoxime methyl ether reacts with phenylhydrazine at 150—160° with evolution of α-methylhydroxylamine, which is absorbed by hydrochloric acid. On cooling, the mass solidifies and consists of anisaldehyde hydrazone and a little resin.

A mixture of β-benzaldoxime ethyl ether (which melts at 82—83°, not at 81—82°) and phenylhydrazine in molecular proportion liquefies at 80°, and then solidifies. On washing the mass with ether, the hydrazone of benzaldehyde remains undissolved, whilst the ethereal filtrate yields a precipitate of β-benzylhydroxylamine hydrochloride melting at 102° if dry hydrogen chloride is passed into it. The original benzyl ether is regenerated on treating the latter with benzaldehyde.

Ethers of β-aldoximes react much more readily with phenylhydrazine than those of the α-aldoximes. W. J. P.

Action of Phenylhydrazine on the Benzoyl Derivatives of some α-Aldoximes. By G. Minunni and G. Corselli (*Gazzetta*, **22**, ii, 164—173; compare preceding abstract).—On mixing ethereal solutions of benzoic chloride and α-benzaldoxime in molecular proportion, *benzoyl-α-benzaldoxime* separates; hydrogen chloride is evolved, and after some hours the deposit is collected, washed with ether, and crystallised from boiling absolute alcohol. It forms very beautiful, brilliant needles, melting at 101—102°; the ethereal washings contain the benzoyl derivative and benzoic acid. A mixture of benzoyl-α-benzaldoxime and phenylhydrazine in molecular proportion liquefies below 100°, and then solidifies to a mixture of benzoylphenylhydrazine and the hydrazone of benzaldehyde, which may be resolved by extracting the latter compound with cold benzene. The same products are formed if 2 mol. proportions of phenylhydrazine are employed to 1 of the benzoyl derivative.

Benzoyl-α-anisaldoxime, prepared in a similar manner to the preceding compound, crystallises from boiling dilute alcohol in shining, white laminæ melting at 109—110°. On heating it with phenylhydrazine in molecular proportion for several hours on the water-bath, ammonia is evolved, and the mass solidifies on cooling. When treated with benzene in the cold, the hydrazone of anisaldehyde dissolves, whilst benzoylphenylhydrazine remains.

Benzoyl-α-metanitrobenzaldoxime crystallises in white laminæ; it melts at 161°, and separates on mixing ethereal solutions of equivalent

quantities of benzoic chloride and α-metanitrobenzaldoxime. On heating it with phenylhydrazine for several hours on the water-bath, ammonia is evolved, and the product crystallises out on cooling. Benzene extracts metanitrobenzaldehyde from the product, leaving a residue of benzoylphenylhydrazine. W. J. P.

Formation of Benzonitrile from α-Benzaldoxime. By G. Minunni (*Gazzetta*, **22**, ii, 174—183).—In the preparation of benzoyl-α-benzaldoxime by the action of benzoic chloride on α-benzaldoxime in ethereal solution (see preceding abstract), the benzoyl derivative gradually separates as a white powder, hydrogen chloride being liberated after a time. If the ethereal solution containing the precipitate and the hydrogen chloride is allowed to remain for 8 to 10 days, the whole redissolves, and, on concentrating the solution, benzoic acid separates; on extracting the ethereal solution from which this has separated with sodium carbonate solution, and distilling off the ether, benzonitrile remains. This decomposition is due to the hydrogen chloride, for, on passing dry hydrogen chloride into ether containing benzoyl-α-benzaldoxime in suspension at −10°, the hydrolysis proceeds quantitatively.

On preparing acetyl-α-benzaldoxime by mixing ethereal solutions of α-benzaldoxime and acetic chloride in the requisite proportion and leaving the liquid to itself for 10 days, then agitating with soda, and adding hydrochloric acid to the solution, a precipitate of benzoic acid formed from the benzonitrile is obtained. The author proves that complete hydrolysis of the acetyl derivative occurs, with formation of acetic acid and benzonitrile, by preparing the acetyl-α-benzaldoxime in a freezing mixture, allowing the solution to remain for 20 days, and evaporating the ether at ordinary temperatures, when a residue of benzonitrile is obtained.

If an ethereal solution of acetyl-α-benzaldoxime, prepared from acetic chloride and α-benzaldoxime, is treated with dry hydrogen chloride at −10°, kept for a month at the ordinary temperature, and the ether then evaporated in a current of dry air, a crystalline residue is left. This, doubtless, contains an additive product of benzonitrile and hydrogen chloride, $CCl_2Ph{\cdot}NH_2$, for, on boiling it with aqueous ammonia in a reflux apparatus, a little benzonitrile remains undissolved, whilst benzamide and benzoic acid are obtained on extracting the ammoniacal solution with ether and concentrating the ethereal solution. W. J. P.

Isomerism of Oximes. By G. Minunni (*Gazzetta*, **22**, ii, 191—212).—The author considers that he has demonstrated the futility of the stereochemical hypotheses offered by Auwers, V. Meyer, Hantzsch, and Werner for elucidating the isomerism of the oximes, his own theory being the only one which accords with the facts. He has shown that Hantzsch's first attack (Abstr., 1891, 823) on his theory was based on misapprehension (Abstr., 1892, 291), whilst the constitutional formulæ assigned by Claus are insufficient to explain the isomerism. W. J. P.

Formation of Hydrogen Nitride (Azoimide) from Aromatic Azoimides. By E. NOELTING, E. GRANDMOUGIN, and O. MICHEL (*Ber.*, **25**, 3328—3342; compare Abstr., 1891, 1473).—*Paranitrodiazobenzeneimide*, $NO_2 \cdot C_6H_4 \cdot N < \overset{N}{\underset{N}{|}}$, is prepared by adding a solution of diazotised paranitraniline to bromine (1 mol.), dissolved in a concentrated solution of potassium bromide (at least 1 mol.), when the *diazoperbromide* separates as a voluminous yellow precipitate, which, after being collected and washed with water at 0°, is added in small quantities, with stirring, to aqueous ammonia, kept cool meanwhile by the addition of ice. The compound is collected, washed, and crystallised from dilute alcohol, when it is obtained in bright yellow, lustrous leaflets; in the pure state, however, it is white, but soon becomes yellow on exposure to light. It is volatile with steam, melts at 74°, and is readily soluble in alcohol, ether, and benzene, but only very sparingly in hot water; on reduction with tin and hydrochloric acid, it yields paraphenylenediamine.

When paranitrodiazobenzeneimide (1 part) is added by degrees to a solution of potassium hydroxide (1 part) in absolute alcohol (10 parts), it dissolves, forming a deep-red solution; this is gently boiled on the water-bath for 48 hours, two-thirds of the alcohol distilled off, and the residue, after acidifying with dilute sulphuric acid, again distilled, when azoimide passes over with the alcohol and water vapour. The distillate is neutralised with alkali, evaporated to dryness, the residue dissolved in water, and the solution acidified and distilled, when an aqueous solution of azoimide, representing about 40 per cent. of the theoretical yield, is obtained. The operation is quite free from danger. A black carbonaceous mass (see below) is present in the residue from the first distillation; it is collected, and from the filtrate paranitraniline is isolated. The formation of the last-named compound accounts for the low yield of azoimide. (Compare also Tilden and Millar, Proc., 1892, 215.)

On extracting the above-mentioned carbonaceous substance with boiling alcohol for several days, and crystallising it from the same solvent, Gattermann and Ritschke's parazophenetoïl, melting at 136° (see Abstr., 1890, 1120), is obtained; but paranitrophenol is apparently not a product of the action. This reaction may serve as a lecture experiment for the preparation of azoimide. When, for example, crude paranitrodiazobenzeneimide is heated on the water-bath for five minutes with 40 per cent. alcoholic potash, 25 per cent. of the calculated quantity of azoimide passes over.

Diorthobromoparanitrodiazobenzeneimide, $NO_2 \cdot C_6H_2Br_2 \cdot N < \overset{N}{\underset{N}{|}}$, is prepared by diazotising diorthobromoparanitraniline (Wurster and Noelting, this Journal, 1875, i, 389), the mixture being kept in a cool place for six days, when it is poured into water at 0°, and bromine added; the precipitated *perbromide* is dropped into aqueous ammonia, and the *bromonitrodiazobenzeneimide* crystallised from dilute alcohol, and subsequently distilled with steam, when it is obtained quite colourless. It crystallises in long, white needles, becomes bluish-

green on exposure to light, melts at 68°, and is readily soluble in alcohol and benzene. On reduction with tin and hydrochloric acid, it gives the corresponding *paradiamine*, $C_6H_2Br_2(NH_2)_2$, which crystallises from hot water in long white, silky needles, melts at 138°, and yields an *acetyl* derivative melting at 108°.

When the pure dibromoparanitrodiazobenzeneimide is heated with 10 per cent. alcoholic potash, in the manner already mentioned, for about 40 hours, 80—85 per cent. of the theoretical amount of azoimide is obtained on distillation, and a solid carbonaceous mass remains in the flask; if this is pulverised and distilled with steam for several days, a compound melting at 190—195° slowly passes over. This, on treatment with hot alkali, is partially dissolved, and, on cooling, yellow needles separate consisting of the sodium derivative of diorthobromoparanitrophenol* (m. p. 141°); the *acetyl* derivative of this compound melts at 178·5°. The portion insoluble in alkali is crystallised from alcohol, and thus proves to be diorthobromoparanitraniline, whilst from the alcoholic mother liquors a compound melting at 105—115° is isolated. Finally, by extracting the carbonaceous substance, after all the volatile matter from it has been driven over with steam, tetrabromazoxyphenol (m. p. 155—156°) is obtained.

Metanitrodiazobenzeneimide is prepared in the same manner as its analogues; it crystallises from dilute alcohol in long, white needles, melts at 55°, is readily volatile with steam, and dissolves in alcohol, benzene, and ether, but is insoluble in water. It does not yield azoimide, even when heated with very concentrated alcoholic potash in a sealed tube.

Orthonitrodiazobenzeneimide, prepared in a similar manner to the para-compound, crystallises from a mixture of benzene and alcohol in long, broad needles, melts at 51—52°, and decomposes at 75—80° yielding a compound melting at 65—67°. It gives less than 30 per cent. of the theoretical amount of azoimide, which distils over, together with orthonitraniline, whilst a compound melting at 98° can be isolated from the carbonaceous residue remaining in the flask.

Orthoparadinitrodiazobenzeneimide, $C_6H_3(NO_2)_2{\cdot}N<\overset{N}{\underset{N}{|}}$, is obtained from 2 : 4-dinitraniline as a brownish-red powder, but on crystallising it from alcohol it decomposes into a compound melting at 68°, and containing less nitrogen. It gives 50—55 per cent. of the theoretical quantity of azoimide on being heated with alcoholic potash, whilst 2 : 4-dinitrophenol is obtained from the non-volatile product of the reaction.

Metanitrorthodiazotolueneimide, $NO_2{\cdot}C_6H_3Me{\cdot}N<\overset{N}{\underset{N}{|}}$, prepared from metanitrorthotoluidine (m. p. 128°), crystallises from dilute alcohol in lustrous, white needles, and melts at 73°. When heated with alcoholic potash, it yields about 30 per cent. of the theoretical amount of azoimide, together with metanitrorthotoluidine.

* The authors here note the interesting fact thus brought to light, namely, that dibromoparatritrophenol is volatile with steam, whereas paranitrophenol is non-volatile.

Orthonitroparadiazotolueneimide, obtained from orthonitroparatoluidine (m. p. 77·5°), forms white, lustrous needles, and melts at 69—70°; it does not yield azoimide on treatment with alcoholic potash.

Paranitrorthodiazotolueneimide, prepared from paranitrorthotoluidine (m. p. 107°), crystallises in long, white, lustrous needles, melts at 68°, and does not give azoimide on treatment with alcoholic potash.

Metanitrodiazometaxyleneimide, from nitrometaxylidine,

$$[Me_2 : NH_2 : NO_2 = 1 : 3 : 4 : 6]$$

(m. p. 123°), crystallises from dilute alcohol in thick, white needles, melts at 75°, and yields no azoimide on treatment with alcoholic potash.

It may be mentioned, finally, that diazobenzeneimide does not give azoimide on treatment with alcoholic potash, even under pressure, but tribromodiazobenzeneimide yields a small amount of azoimide. By this work it is seen that only those nitro-derivatives yield azoimide which contain the nitro-group in a para- or ortho-position relatively to the diazoimido-group. A. R. L.

New Method of preparing Benzoic Anhydride. Formation of Dehydracetic acid from Acetic Chloride. By G. Minunni (*Gazzetta*, **22**, ii, 213—217).—The reaction occurring between pyridine and acetic chloride, resulting in the conversion of the latter into dehydracetic acid, is explained by Feist on the assumption that dehydracetic acid is the product of the direct condensation of acetic chloride, and that the pyridine assists the reaction by combining with the liberated hydrogen chloride. This induced the author to examine the action of other acid chlorides on pyridine in order to obtain confirmation of this view.

On mixing ethereal solutions of benzoic chloride and pyridine, a white, deliquescent substance separates, which yields benzoic chloride and pyridine when treated with water. If no solvent is used, a slight rise in temperature is noted on mixing benzoic chloride and pyridine, an additive product being formed; whilst the liquid rapidly darkens and deposits a little pyridine hydrochloride. After a time, however, a considerable quantity of a white, deliquescent substance separates, and on treating this or the mother liquor with water, pure benzoic anhydride is precipitated, the pyridine remaining in the aqueous solution as hydrochloride. On adding water to the mixture half an hour after its preparation, 78 per cent. of the theoretical yield of pure benzoic anhydride may be obtained. This is, therefore, the most convenient and economical method known of preparing the anhydride.

The action of acetic chloride on pyridine may be explained in a manner similar to the above; the white substance first deposited is an additive product, and on treatment with water yields acetic anhydride, which at the moment of its formation condenses to form dehydracetic acid. W. J. P.

Heptanaphthenic (Hexahydrobenzoic) acid. By V. Markovnikoff (*Ber.*, **25**, 3355—3366; compare Abstr., 1892, 714, and Aschan, 1891, 1053, 1481; 1892, 847; and this vol., i, 33).—Benzoic acid was reduced by pouring a solution of it in a high-boiling alcohol (amyl, capryl, or octyl) upon melted sodium contained in a large round-bottomed flask, heating the mixture until all the sodium had disappeared, adding the equivalent amount of dilute sulphuric acid, removing the alcoholic solution, drying it by distilling off the water, and repeating the process 3—4 times with fresh sodium. The final product was then fractionated, and the pure acid obtained by freezing the fractions, pressing the crystals between filter-paper, and recrystallising from hot water. *Heptanaphthenic acid* melts at 28·5—29·5°, and boils at 234·5—235° under 750 mm. pressure. Its odour resembles that of both valeric acid and ethyl oxalate. The crystals deliquesce in the air, dissolve very readily in alcohol, ether, chloroform, benzene, and light petroleum, but only slightly in cold water, and are but little volatile with steam. The acid does not take up bromine, but decolorises permanganate rather rapidly.

The *sodium salt* forms crusts of transparent, efflorescent needles. The *calcium salt*, $(C_7H_{11}O_2)_2Ca + 5H_2O$, forms long needles; a basic salt was also obtained. The *barium salt*, $(C_7H_{11}O_2)Ba + 2\frac{1}{2}H_2O$, crystallises in bundles of small needles. The *magnesium salt* is very soluble, and forms crystalline crusts, which effloresce and form brilliant, white scales. The very characteristic *zinc salt* crystallises in brilliant scales or flattened needles, and is much more soluble in cold than in hot water. The *cadmium salt* is more soluble in hot water, but otherwise resembles the zinc salt. The *lead salt* forms a white precipitate which separates from water in small needles, or as a gelatinous crust. The *silver salt*, $C_7H_{11}O_2Ag$, forms a white precipitate, which, when dry, is but little affected by light. The *methyl salt* boils at 181—183° under 750 mm. pressure, and has a sp. gr. at $0°/0° = 1·0431$, at $20°/20° = 0·9864$; its odour resembles that of ethereal salts of fatty acids. The *amide*, $C_6H_{11}·CONH_2$, crystallises in quadrangular plates, which group themselves in needles; it melts at 185—188°, and is but slightly soluble in water. When heptanaphthenic acid is heated at 290° with anhydrous copper sulphate, it is partly oxidised to benzoic acid, but some benzophenone is also formed.

Other unsaturated hydrobenzoic acids are also obtained when benzoic acid is reduced with sodium, but the study of them is left to Aschan. The latter's results respecting hexahydrobenzoic acid and its derivatives are criticised, and in cases of difference the author upholds his own figures, maintaining that he has worked with purer materials. C. F. B.

Separation of Phenyldibromopropionic acid into its Optically Active Modifications. By L. Meyer, Jun. (*Ber.*, **25**, 3121—3123).—Freshly prepared and finely divided strychnine (1 mol.) is mixed with 20 times its weight of alcohol (92 per cent.), and phenyldibromopropionic acid (1 mol.) dissolved in alcohol is added; a clear solution is obtained, which after a short time deposits

well-formed, colourless crystals of the lævo-acid. The dextro-acid remains in the mother liquor, and does not crystallise so well.

Strychnine lævo-phenyldibromopropionate, $C_{21}H_{22}N_2O_2,C_9H_8Br_2O_2$, begins to decompose at 80°, and is insoluble in water. The *lævo*-acid is obtained by rubbing the salt with very dilute hydrochloric acid until the insoluble residue shows no trace of strychnine. It is then crystallised from alcohol. It has all the properties of the inactive acid, but has a specific rotatory power $[\alpha]_D = -13{\cdot}1$.

The *dextro*-acid is obtained from the mother liquor, and has a specific rotatory power $[\alpha]_D = +14{\cdot}0$. E. C. R.

Sulphonephthaleïns. By C. C. Blackshear (*Amer. Chem. J.*, 14, 455—473).—Commercial "saccharin" (50 grams) is boiled in a reflux apparatus for three quarters of an hour with dilute hydrochloric acid (1 to 12), the parasulphaminebenzoic acid which crystallises out on cooling is separated, the filtrate evaporated to dryness at 100°, and the residue is taken up with cold water and evaporated to crystallisation. The acid ammonium orthosulphobenzoate, $COOH{\cdot}C_6H_4{\cdot}SO_2{\cdot}ONH_4$, thus obtained (compare Remsen and Burton, Abstr., 1890, 94; 15 grams), is heated with resorcinol (12 grams) at 170—175°, and stirred until water ceases to be evolved, when ammonium dihydroxybenzoylbenzenesulphonate,

$$C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}ONH_4,$$

separates in yellow, silky crystals, which gradually lose their colour on purification. The ammonium salt is converted into a *basic lead salt* by digestion with litharge in concentrated aqueous solution, and the acid liberated by hydrogen sulphide from the acetic acid solution of the lead salt. Dihydroxybenzoylbenzenesulphonic acid, with $3H_2O$ (compare Remsen and Linn, Abstr., 1889, 710), crystallises in small, colourless, apparently monoclinic plates. The *barium salt*, with $6H_2O$, crystallises in small, colourless plates; the *calcium salt*, with $4H_2O$, and the *silver salt*, with $2H_2O$, in radial groups of colourless needles; and the *normal lead salt*, with $7H_2O$, in small, colourless rhombohedra or long needles. Attempts to form an ethyl salt and an acetyl derivative, and to displace the hydroxyl groups by chlorine by the action of phosphoric chloride, were unsuccessful. When the acid is heated with concentrated nitric acid, it yields trinitroresorcinol and orthosulphobenzoic acid. When heated with concentrated sulphuric acid at 160—180°, it is converted into sulphonefluoresceïn, which is collected, washed with cold water, dissolved in aqueous potassium hydroxide, and reprecipitated by dilute sulphuric acid.

Jn. W.

The Indoxazen Group. By W. R. Cathcart, Jun., and V. Meyer (*Ber.*, **25**, 3291—3297).—In the course of their work on the oximes of substituted benzophenone, the authors have prepared considerable quantities of paradibromobenzophenone from parabromobenzoic chloride and bromobenzene; on one occasion, however, a compound was formed, which crystallised in small plates, melted at

142°, and contained 29 per cent. of bromine. It readily yielded an *oxime*, which was deposited from alcohol in colourless crystals melting at 156—159°.

Orthobromobenzophenone oxime has been previously described (Abstr., 1892, 992); it is prepared by the action of hydroxylamine on the ketone in alkaline solution at ordinary temperatures, or by heating the ketone with hydroxylamine hydrochloride in alcoholic solution at 130°; it crystallises from alcohol in large prisms, which melt at 76—132°; the anhydrous compound melts at 132—133°. No isomeric oxime could be detected.

Phenylindoxazen has also been described (*loc. cit.*); it boils at 331—336° with slight decomposition; its formation appears to be due to the presence of two negative (phenyl) groups linked to the same carbon atom, since the oximes of orthobromobenzaldehyde and of orthobromoacetophenone do not yield indoxazen derivatives; orthobromobenzoic hydrazone behaves in a similar manner (compare Russanow, next abstract).

Phenylindoxazen is not acted on by concentrated hydrochloric acid at 200°. A *dinitro-derivative*, $C_{13}H_7ON(NO_2)_2$, is obtained by adding powdered phenylindoxazen in small quantities to concentrated nitric acid, which is cooled with ice; the solution is quickly poured into a large volume of ice-cold water, and the deposited product purified by repeated crystallisation from glacial acetic acid; it is colourless, and melts at 239—241°.

No well characterised base could be obtained by the reduction of the above compound. J. B. T.

Indoxaxen Derivatives. By A. Russanow (*Ber.*, **25**, 3297—3302).—It has been shown (preceding abstract) that the formation of indoxazen derivatives only proceeds when the group $C_6H_4Br{\cdot}CH{:}NOH$ is linked to a second negative group; orthobromophenylglyoxylic acid, $C_6H_4Br{\cdot}C(NOH){\cdot}COOH$, does not, however, yield indoxazencarboxylic acid, but decomposition products of this substance.

Orthobromobenzoic chloride, $C_6H_4Br{\cdot}COCl$, prepared from orthobromobenzoic acid and phosphoric chloride, is heated with 0·8 part of anhydrous silver cyanide in a sealed tube for 24 hours at 100°; the product is extracted with anhydrous ether, the solution evaporated, and the residual *cyanide* purified with light petroleum, from which it crystallises in yellow prisms melting at 62—64°.

Orthobromobenzoylformamide, $C_6H_4Br{\cdot}CO{\cdot}CONH_2$, is obtained by treating the cyanide with concentrated hydrochloric acid at the ordinary temperature; the reaction requires 24—48 hours for completion. The amide is soluble in about 5 parts of hot water, and crystallises in flat needles or plates melting at 136—137°. The yield is 85 per cent. of the cyanide employed.

Orthobromobenzoylformic acid, $C_6H_4Br{\cdot}CO{\cdot}COOH$, is formed by heating the amide (8·5 grams) dissolved in water (155 c.c.) with potassium hydroxide (2·1 grams) dissolved in water (45 c.c.), until evolution of ammonia ceases; the solution is acidified with hydrochloric acid, extracted with ether, and, after the removal of this, the

acid readily crystallises, and melts at 93—103°. The yield is 8 grams from the above quantities.

Orthobromisonitrosophenylacetic acid, $C_6H_4Br\cdot C(NOH)\cdot COOH$, is prepared from the preceding compound by the action of hydroxylamine in a feebly alkaline solution at the ordinary temperature; it crystallises from warm (not boiling) water in small, colourless needles, which melt at 162—164°, with decomposition. The impure oxime, on treatment with soda, yields resinous products, but on heating the crystallised compound for two hours with excess of soda (1 to 4), salicylic acid is obtained; in all probability the reaction proceeds in several stages. Indoxazencarboxylic acid,

$$C_6H_4<\begin{matrix}C\text{—}\\O\cdot N\end{matrix}>C\cdot COOH,$$

is first formed; from this carbonic anhydride is eliminated, and the resulting indoxazen, $C_6H_4<\begin{matrix}CH\\O\text{—}\end{matrix}>N$, thus formed then changes into the nitrile, $OH\cdot C_6H_4\cdot CN$, which, on hydrolysis, yields salicylic acid. The reaction is therefore analogous to the conversion of phenylisoxazole into benzoylacetic nitrile.

The fact that indoxazen is so unstable, whilst the phenyl derivative is not acted on by either acids or alkalis, is explained by the presence of a "wandering" hydrogen atom in the former compound.

J. B. T.

Orthodiamidodiphenyl. By E. Täuber (*Ber.*, **25**, 3287—3290).—Diorthamidodiphenyl combines with benzile in the same way as a true orthodiamine, and yields a compound of the formula

$$\begin{matrix}C_6H_4\cdot N{:}CPh\\ |\\C_6H_4\cdot N{:}CPh\end{matrix} \quad \text{or} \quad \begin{matrix}C_6H_4\cdot N\cdot CPh\\ |\ \ \ \

agents, and when treated with ferric chloride or chromic acid, it is completely destroyed. E. C. R.

Oximes of certain Symmetrical Benzophenones. By W. R. CATHCART, Jun. (*Ber.*, **25**, 3302—3303; compare this vol., i, 94).—Paradibromobenzophenone forms only one oxime melting at 151°; the oxime of paradimethylbenzophenone also exists in only one modification. *Paradimethoxybenzophenone* is prepared from paramethoxybenzoic chloride and methoxybenzene, and crystallises in colourless needles or plates which melt at 144—145°. The *oxime* is deposited from alcohol in colourless needles melting at 133—134°. No isomeric compound could be detected.

The following compounds appear to yield only one oxime:—Meta- and para-dibromobenzophenone, paradichlorobenzophenone, paradiiodobenzophenone, paradimethylbenzophenone, paradimethoxybenzophenone. The corresponding para- and meta-*mono*-derivatives each yield two oximes; some of the ortho-compounds form only one oxime, whilst in the case of others the isolation of a second modification is a matter of difficulty. J. B. T.

Benzileoximes. By G. MINUNNI and G. ORTOLEVA (*Gazzetta*, **22**, ii, 183—190).—γ-Benzileoxime does not react with phenylhydrazine in a salt-water bath; reaction, however, occurs at 110—120°, ammonia is evolved, the mass liquefies, and, after a time, resolidifies. On washing the product with cold alcohol and crystallising the residue from boiling alcohol, minute, yellow needles of benzile-dihydrazone, melting at 223°, are obtained. The same product is formed on heating α-benzileoxime with phenylhydrazine at 120° until ammonia is no longer evolved; the mass is completely soluble in hot alcohol, but the dihydrazone separates after several days.

α-Benziledioxime (5 grams), when heated with phenylhydrazine (4·5 grams) at 150—160°, gives off ammonia, and, by treating the cooled mass with alcohol, unaltered dioxime and benziledihydrazone are obtained. On heating the dioxime (2 grams) with a large excess (10 grams) of phenylhydrazine at 170° for some hours, complete conversion into β-benziledioxime occurs; the latter then combines with the phenylhydrazine, forming a compound of the composition $\begin{matrix}\mathrm{PhC{\cdot}NH(OH)}\\ \mathrm{PhC{\cdot}NH(OH)}\end{matrix}\!>\!\mathrm{N{\cdot}NHPh}$, which melts at 149°. On treating this with acids, it yields β-benziledioxime and phenylhydrazine.

W. J. P.

α-Benzilephenylhydrazine and the Oxidation of the Hydrazones. By G. MINUNNI (*Gazzetta*, **22**, ii, 217—230).—α-Benzilephenylhydrazine is readily formed on heating a mixture of benzyl chloride (1 mol.) and phenylhydrazine (2 mols.) at 120° for some hours. Water is then added, and the mass heated on the water-bath, when phenylhydrazine hydrochloride dissolves, whilst the substituted hydrazine separates as an oil. This is extracted with ether, and the ethereal solution shaken with dilute hydrochloric acid; on evaporat-

ing the aqueous solution on the water-bath and adding concentrated hydrochloric acid, the hydrochloride separates in white needles which yield the free base on treatment with potash. α-Benzilephenylhydrazine is an oil which does not crystallise on cooling, as has been stated. It decomposes and gives off ammonia on heating, and at 250° a yellowish-brown oil distils which gives a white, crystalline compound with benzaldehyde; this melts at 190—192°, and is sparingly soluble in ether.

α-Benzilephenylhydrazine hydrochloride crystallises from water in white needles, melts at 166—167°, and is much less stable than phenylhydrazine hydrochloride. It decomposes on heating with water, and, on treating its aqueous solution with sodium acetate solution, the free base separates. The *acetyl* derivative melts at 121—122°, and is readily soluble in hot xylene, giving a solution which dissolves sodium with evolution of hydrogen. The *benzoyl* derivative forms beautiful, white needles melting at 139—140°, and is readily soluble in the ordinary solvents.

On adding yellow mercuric oxide to a dilute chloroform solution of α-benzilephenylhydrazine, a slight rise of temperature occurs; after filtering and concentrating the solution, a *tetrazone*,

$$CH_2Ph{\cdot}NPh{\cdot}N{:}N{\cdot}NPh{\cdot}CH_2Ph,$$

separates, and crystallises from alcohol in colourless laminæ which melt with decomposition at 142°. The substance obtained by Michaelis and Phillips in needles melting at 109° could not be got. If a concentrated chloroform solution of α-benzilephenylhydrazine is treated with mercuric oxide, violent action occurs, and, on evaporating off the solvent and crystallising the product from alcohol, the tetrazone melting at 142° is obtained, together with a crystalline substance, more soluble in alcohol, which melts at 103—104°; the latter gave no satisfactory numbers on analysis.

On cautiously heating the hydrazone of benzaldehyde with yellow mercuric oxide on the water-bath, vigorous action occurs; the solution if filtered, concentrated, and left to crystallise, yields a substance which melts at 179—180°, and probably has the composition $CHPh{:}N{\cdot}NPh{\cdot}NPh{\cdot}N{:}CHPh$. It crystallises from benzene in beautiful, yellow needles, and is very sparingly soluble in hot alcohol. Mercuric oxide reacts with the hydrazone of metanitrobenzaldehyde, yielding a substance melting at 155°; this is still under examination.

Paranitrobenzile chloride does not act on phenylhydrazine in the cold, but, on heating, vigorous action sets in and a resin is obtained. Ethylene bromide only acts on phenylhydrazine on heating; at about 90°, reaction occurs with explosive violence, the flask being shattered. A mixture of monochloracetal and phenylhydrazine gives off ammonia at 140°. On mixing ethereal solutions of chlorethyl oxide and phenylhydrazine, white laminæ of an unstable substance melting at 121° are obtained. W. J. P.

Derivatives of α- and β-Naphthylamine containing Asymmetrical Nitrogen and Carbon Atoms. By C. A. Bischoff

and A. HAUSDÖRFER (*Ber.*, **25**, 3263—3270).—*Diacetyldi-α-naphthylethylenediamine*, $C_2H_4(NAc\cdot C_{10}H_7)_2$, is obtained by warming a mixture of dinaphthylethylenediamine and acetic chloride. It crystallises in small, colourless tablets, melts at 239—241°, and is soluble in chloroform and hot acetic acid, and only sparingly so in other solvents.

Dimonobromacetyldi-α-naphthylethylenediamine is obtained by treating di-α-naphthylethylenediamine, dissolved in benzene, with bromacetic bromide; it crystallises in colourless, four-sided prisms, melts at 215° with decomposition, is insoluble in water, ether, carbon bisulphide, acetone, light petroleum, dilute mineral acids, alkalis, and cold acetic acid, and sparingly soluble in chloroform and benzene, more so in hot alcohol.

Di-α-naphthylethylenediamine hydrobromide, $C_{22}H_{22}N_2Br_2$, is obtained as a bye-product in the preparation of the above and following compounds. It crystallises in faintly coloured aggregates, melts at 205—207°, is insoluble in ether and benzene, and easily soluble in hot chloroform and alcohol.

Di-α-bromopropionyldi-α-naphthylethylenediamine, obtained in a similar way to the above compounds, crystallises in long, four-sided prisms, melts at 216°, and is easily soluble in carbon bisulphide, chloroform, and acetic acid. In one experiment, in which a large excess of acid bromide was employed in the formation of this compound, di-α-naphthylethylenediamine monhydrobromide, $C_{22}H_{21}N_2Br$, was obtained. This is also obtained by boiling the dihydrobromide with alcohol; it crystallises from alcohol in slender needles, melts at 236—237°, and is soluble in hot acetic acid.

Di-α-bromonormalbutyryldi-α-naphthylethylenediamine crystallises in long, four-sided prisms, and melts at 233—234°.

Di-α-bromisobutyryldi-α-naphthylethylenediamine melts at 197°, and resembles the preceding normal compound in crystalline form and solubility.

Di-β-naphthylcarbamide, $CO(NH\cdot C_{10}H_7)_2$, is obtained by adding carbonyl chloride dissolved in toluene to an ethereal solution of β-naphthylamine. It crystallises from nitrobenzene in slender needles, melts at 295°, and is insoluble in the ordinary solvents.

Oxaldi-β-naphthalide, $C_2O_2(NH\cdot C_{10}H_7)_2$, is obtained by heating a mixture of oxalic acid and β-naphthylamine at 265°. It crystallises in colourless tablets, melts at 276°, and is sparingly soluble in the ordinary solvents. When heated with 2—3 mol. proportions of alcoholic potash, it is decomposed into oxalic acid and naphthylamine. If however, only 1 mol. proportion of potash is employed, it yields an acid which is probably β-naphthyloxamic acid, $C_{10}H_7NH\cdot CO\cdot COOH$, and melts at 179°.

Succindi-β-naphthalide, $C_4H_4O_2(NH\cdot C_{10}H_7)_2$, is obtained by heating a mixture of β-naphthylamine (24 grams) and succinic acid (10 grams) at 190—200° for one hour. The product, which contains β-dinaphthylamine (m. p. 172°), is extracted with water, acetic acid, and alcohol, and then crystallised from nitrobenzene. It is a colourless, microcrystalline substance, melts at 266°, and is insoluble in all the ordinary solvents, except concentrated sulphuric acid.

Diacetyldi-β-naphthylethylenediamine is obtained by heating di-β-naphthylethylenediamine with acetic anhydride at 150—175°. It crystallises from alcohol in small, colourless tablets, melts at 175—176°, and is insoluble in water and light petroleum.

Dimonobromacetyldi-β-naphthylethylenediamine is obtained, together with di-β-naphthylethylenediamine hydrobromide, by the action of bromacetic bromide on di-β-naphthylethylenediamine dissolved in benzene. It crystallises in colourless, microscopic needles, and melts at 144°.

Di-α-bromopropionyldi-β-naphthylethylenediamine crystallises with 1 mol. of benzene in thin, colourless prisms, and, after drying at 100°, melts at 196—197°.

Di-α-bromonormalbutyryldi-β-naphthylethylenediamine crystallises in slender, white needles, and melts at 180°.

Dibenzoyldi-β-naphthylethylenediamine is obtained, together with di-β-naphthylethylenediamine hydrochloride, by heating a mixture of di-β-naphthylethylenediamine (18 grams), benzene (300 grams), and benzoic chloride (30 grams) in a reflux apparatus for 15 hours. It crystallises in small, lustrous needles, melts at 202—203°, and is soluble in chloroform, hot acetic acid, carbon bisulphide, and benzene, sparingly soluble in acetone and cold benzene. E. C. R.

Action of β-Naphthol on Formaldehyde. By H. Hosaeus (*Ber.*, **25**, 3213—3215).—When a tolerably concentrated solution of β-naphthol in glacial acetic acid is boiled with about an equal volume of commercial formaldehyde solution, *methylenedi-β-naphthol*, $CH_2(C_{10}H_6{\cdot}OH)$, is formed. This crystallises in microscopic needles, melts at 188°, and is soluble in cold, dilute aqueous soda. The *diacetyl* derivative crystallises in needles melting at 214°.

Methylenedihydroxynaphthoic acid, $C_{23}H_{16}O_6$, was obtained by boiling a solution of β-hydroxynaphthoic acid with formaldehyde solution, with the addition of a few drops of dilute sulphuric acid. It crystallises in golden-yellow needles, insoluble in glacial acetic acid, alcohol, ether, benzene, and water. At 280° it blackens without melting. L. T. T.

Terpenes from Resins. By O. Wallach and T. Rheindorff (*Annalen*, **271**, 308—311).—When copal is distilled, the oily distillate washed with soda and distilled with steam, a mobile liquid boiling at 40—350° is obtained. The lowest boiling fractions of this liquid seem to contain isoprene; the portions boiling at 154—164° consist principally of a hydrocarbon of the composition $C_{10}H_{16}$ which was proved to be pinene, and the fractions boiling at about 175° were found to contain dipentene (compare Friedburg, *J. Amer. Chem. Soc.*, 1890, 285).

The presence of pinene in the oil obtained by the dry distillation of commercial olibanum was also proved, whereas the product obtained in like manner from the hard elemi resin was found to contain dextrophellandrene.

The oil obtained by the dry distillation of colophony contains small quantities of pinene and dipentene. F. S. K.

Sesquiterpenes. By O. WALLACH and W. WALKER (*Annalen*, **271**, 285—299).—Some of the sesquiterpenes, $C_{15}H_{24}$, behave in certain respects like some of the ordinary terpenes, and combine directly with 1 mol. H_2O, yielding crystalline compounds of the general formula $C_{15}H_{26}O$, which, when boiled with dilute acids, are reconverted into hydrocarbons by loss of 1 mol. H_2O.

Caryophyllene alcohol, $C_{15}H_{25}\cdot OH$, is best obtained by dissolving caryophyllene (25 grams), boiling at 250—260°, in a mixture of glacial acetic acid (1 kilo.), concentrated sulphuric acid (20 grams), and water (40 grams), and heating the solution for 12 hours on the water-bath. The mixture is then steam-distilled. At first, acetic acid and a mobile oil, having an ethereal odour, pass over, but towards the end of the operation, the alcohol, which is only slightly volatile, collects in the receiver, and gradually solidifies on cooling; it is first spread on porous earthenware, then distilled from a retort, and finally recrystallised from alcohol, from which it separates in well-defined, hexagonal, rhombic, hemihedric crystals melting at 96°. It boils at 287—289° without appreciable decomposition, and dissolves freely in most of the ordinary organic solvents, but is only sparingly soluble in hot, and almost insoluble in cold, water; its vapours have a faint odour recalling that of pine needles. The *chloride*, $C_{15}H_{25}Cl$, prepared by treating the alcohol with phosphorus pentachloride, separates from ethyl acetate and from light petroleum in well-defined crystals, melts at 63°, and boils at 293—294° without decomposition; it is readily soluble in hot, but more sparingly in cold, alcohol. The *bromide*, $C_{15}H_{25}Br$, is formed when the alcohol is treated with phosphorus tribromide, or with phosphorus and bromine in carbon bisulphide solution; it separates from alcohol in rhombic crystals, and melts at 61—62°. The *iodide*, $C_{15}H_{25}I$, prepared in like manner, crystallises in long, colourless needles or rhombic prisms, and melts at 61°; it decomposes when heated. The *nitrate*, $C_{15}H_{25}O\cdot NO_2$, can be obtained by mixing the alcohol with a very small quantity of ethyl alcohol, and gradually adding excess of fuming nitric acid to the well-cooled mixture; on keeping for some time at the ordinary temperature, the ethereal salt is deposited in colourless needles, and a further quantity of the same substance is precipitated, but in an impure condition, on diluting the acid mother liquors. It crystallises in rhombic prisms, melts at 96°, and is soluble in alcohol, ether, and benzene; it is very stable, and is not acted on to any appreciable extent by boiling alcoholic potash or by a boiling alcoholic solution of sodium ethoxide, but, when heated with concentrated alcoholic potash at 150°, it is decomposed with formation of the alcohol. This ethereal salt seems also to be formed when a concentrated alcoholic solution of the chloride is treated with fuming nitric acid at a temperature below 70°.

All the compounds described above are optically inactive, and are extremely stable; the chloride seems not to be acted on by boiling aniline.

A *hydrocarbon* of the composition $C_{30}H_{50}$ is formed when the above-mentioned iodide is dissolved in ether and treated at the ordinary temperature with a large excess of sodium in the form of wire; it

boils at 225—230° (13 mm.), and solidifies on cooling to a brittle, transparent mass, which is almost insoluble in alcohol and glacial acetic acid, but readily soluble in ether; it separates from alcoholic ether in small, crystalline nodules, which sinter at 120°, but do not melt completely until the temperature rises to 135°.

Clovene, $C_{15}H_{24}$, is obtained when the alcohol described above is heated for 15 minutes almost to its boiling point with excess of phosphoric anhydride, the product distilled with steam, and again treated with phosphoric anhydride as before. It boils at 261—263°, and its sp. gr. is 0·930 at 18°; its refractive power is $[n]_D = 1·50066$ at 18°, from which the molecular refraction is calculated to be $M = 64·77$, whereas the calculated value for $C_{15}H_{24}$ $\equiv$ is $M = 64·45$. This hydrocarbon cannot be converted into the crystalline alcohol from which it is derived, so that it must be regarded as different from caryophyllene.

An alcohol identical with the compound (m. p. 96°) described above can be obtained from the fraction of oil of copaïva boiling at 250—270° by the method already mentioned; that oil of cloves and oil of copaïva contain the same hydrocarbon is also proved by the fact that a crystalline nitrosochloride, $C_{15}H_{24}NOCl$, can be isolated from both the oils by the usual method; this compound is a colourless, sparingly soluble powder, melts at 161—163° with decomposition, and reacts very readily with piperidine, yielding an oily nitrolamine.

A *hydrocarbon*, which has in all probability the composition $C_{15}H_{28}$, is formed when dihydrochlorosesquiterpene (m. p. 118°) is heated with concentrated hydriodic acid at 200°; it boils at 257—260°, and behaves like a saturated compound; its sp. gr. is 0·872 at 18°, and its refractive power $[n]_D = 1·47439$, or $M = 67·09$, the calculated value for a saturated compound of the composition $C_{15}H_{28}$ being $M = 67·10$.

It is clear from the above experiments that some, at any rate, of the isomeric sesquiterpenes can be sharply distinguished from others; they may, in fact, be divided into two groups, according as they contain two or only one ethylenic linking. The best known representative of the first class is the widely distributed lævorotatory sesquiterpene, which is characterised by the crystalline additive product which it forms with two molecules of the halogen acids; the occurrence of this hydrocarbon in the oils of cubebs, savin, cadinum, betel, camphor, galbanum, patchouli, juniper, asafœtida, coto-bark, and olibanum has been proved. The author proposes the name *cadinene* for this sesquiterpene.

Cadinene contains two double linkings, and differs from caryophyllene in having a rather higher boiling point and in giving crystalline additive products with the halogen acids. Clovene differs from caryophyllene in not combining with water, and in not forming a crystalline nitrosochloride; it seems to contain only one ethylenic linking. The hydrocarbon which generally occurs with cadinene in ethereal oils, and which differs from the latter in not giving crystalline additive products with halogen acids, is also certainly not identical with caryophyllene. The sesquiterpene obtained from patchouli-camphor,

which is better termed patchouli alcohol, must also be regarded as a distinct compound, and is possibly related to cedrene, the sesquiterpene of cedar oil. F. S. K.

Ethereal Oil of Paracoto Bark. By O. WALLACH and T. RHEINDORFF (*Annalen*, **271**, 300—308).—The ethereal oil which is obtained as a bye-product in the separation of the therapeutic constituents occurring in paracoto bark has been previously examined by Jobst and Hesse, according to whom it contains α-paracotene, $C_{12}H_{18}$; β-paracotene, $C_{11}H_{18}$; α-paracotol, $C_{15}H_{24}O$; and β- and γ-paracotol, $C_{28}H_{40}O_2$. A sample of the ethereal oil in question, which had been separated by distillation into "light" and "heavy" oil, was examined by the authors with the following results:—The fractions of lowest boiling point give, when shaken with sodium hydrogen sulphite, a very small quantity of a crystalline substance, which, when treated with dilute sulphuric acid, gives off an odour recalling that of benzaldehyde; this compound could not be characterised, as it is formed in such small quantities. When the portions of light oil which boil at 130—140° are saturated with a glacial acetic acid solution of hydrogen bromide, the mixture being well cooled, a crystalline substance is soon deposited; this compound melts at 121°, has the composition $C_{15}H_{26}Br_2$, and can be readily converted into a hydrocarbon, $C_{15}H_{24}$, which boils at 272°; this hydrocarbon gives a crystalline dihydrochloro-derivative, $C_{15}H_{26}Cl_2$, which melts at 118°, and has a specific rotatory power of $[\alpha]_D = -33{\cdot}5°$ in chloroform solution; these facts prove that the hydrocarbon in question is identical with cadinene (compare preceding abstract).

The fractions of lowest boiling point obtained from the oil of coto bark also contained cadinene.

When the mother liquors from the crystalline dihydrobromo-derivative described above are treated with potash and submitted to steam distillation, an oil passes over; this is acted on readily by bromine in ethereal solution, with evolution of hydrogen bromide and formation of tribromomethyleugenol. The presence of methyleugenol in the coto bark oil is further proved by the fact that, when the "heavy" oil is oxidised with potassium permanganate it yields veratric acid (dimethoxybenzoic acid).

When methyleugenol is dissolved in light petroleum, and treated with an aqueous solution of sodium nitrite and dilute acetic acid, it is converted into a solid, unstable compound, which melts at about 125°, and has the composition $C_3H_5{\cdot}C_6H_3(OMe)_2{\cdot}N_2O_3$. F. S. K.

Essential Oil of Garlic (Allium sativum). By F. W. SEMMLER (*Arch. Pharm.*, **230**, 434—443).—Garlics were found to yield 0·09 per cent. of their weight of a yellow-coloured, optically inactive essential oil, which has the well known intense odour; it sp. gr. at 14·5° is 1·0525. It deposits a small quantity of crystals when cooled in a freezing mixture, does not contain oxygen, and decomposes when heated at 150° (compare Wertheim, *Arch. Pharm.*, 1891, 1). The oil was fractionally distilled under a pressure of 16 mm.

Fraction 1 (6 per cent.) consists of *allylpropyl bisulphide*, $C_3H_5S{\cdot}SPr$, a bright yellow oil of sp. gr. 1·0231 at 15°, boiling at 66—69° (16 mm.), and having the odour of onions; it gives voluminous precipitates with mercuric and auric chlorides, which are sparingly soluble in alcohol, and, when treated with zinc-dust at 130°, yields a *compound*, $C_6H_{13}S$. It is decomposed by oxidising agents with the production of carbonic anhydride, oxalic acid, propionic and lower fatty acids, and sulphuric acid.

Fraction 2 (60 per cent.) is *diallyl bisulphide*, $S_2(C_3H_5)_2$, a light-yellow oil, having the odour of garlic; it is rendered colourless by distilling with a little potassium, when it passes over at 78—80° (16 mm.). It has a sp. gr. at 14·8° = 1·0237, and on reduction with zinc-dust, yields a *compound*, $C_6H_{10}S$, which boils under the ordinary pressure at 135—139°; it also reacts with potassium, decomposes into carbonic anhydride, oxalic, formic, and acetic acids, on oxidation with nitric acid, combines with halogens, and does not react with mercuric oxide, even at 100°.

Fraction 3 (20 per cent.), representing the portion passing over between 112° and 122° (16 mm.), has the empirical formula $C_6H_{10}S_2$, its sp. gr. at 15° being 1·0845; it yields the compound, $C_6H_{10}S$, when heated with zinc dust.

Fraction 4 (10·5 per cent.) consists of the residue boiling above 122° (16 mm.); it decomposes if the distillation is continued. On analysis, values were obtained approximating to those required by the formula $C_6H_{10}S_4$.

Oil of garlic contains, therefore, neither allyl sulphide, as stated by Wertheim (*loc. cit.*), nor a sesquiterpene, as stated by Beckett and Wright (*Jahresb.*, 1878, 398). A. R. L.

Note.—The sesquiterpene, to which the author refers, was obtained by Church from oil of cloves, and examined by Beckett and Wright (this Journal, 1876, i, 6). It is erroneously stated in the *Jahresbericht* (*loc. cit.*) that the terpene was isolated from oil of garlic (Knoblauchöl). A. R. L.

Essential Oil of Onion (Allium cepa, L.). By F. W. Semmler (*Arch. Pharm.*, **230**, 443—448).—Onions yield 0·005 per cent. of their weight of a dark-brown, essential oil, which does not contain oxygen, has a sp. gr. at 8·7° = 1·041, and exhibits a rotation of −5° in a 100 mm. tube; a small quantity of crystals separate on cooling it in a freezing mixture. As it decomposes when distilled at the ordinary pressure, it was fractionated under a pressure of 10 mm.

The main portion of the oil consists of a *compound*, $C_6H_{12}S_2$, an oil of sp. gr. 1·0234 at 12°, which boils at 75—83° (10 mm.), and is converted into the *compound* $C_6H_{14}S_2$ on treatment with potassium; this new compound boils at 68—69° (10 mm.), and seems to be present in small quantity in the original oil. The compound $C_6H_{12}S_2$ is converted by zinc-dust into a monosulphide, $C_6H_{12}S$ (b. p. 130°). A small quantity of a substance was isolated from the fractions boiling above 100° (10 mm.), and appears to be identical with one of the

compounds obtained from oil of asafœtida. The residue boiling above 125° (10 mm.) contains a higher sulphide, and gives the compound $C_6H_{12}S$ on reduction with zinc-dust. Neither allyl sulphide, nor a sesquiterpene, were present. A. R. L.

Menthylamine. By O. Wallach and M. Kuthe (*Ber.*, **25**, 3313—3316).—The preparation of menthylamine from menthone and ammonium formate has been described by Wallach (Abstr., 1892, 500), whilst Andres and Andréeff obtained menthylamine by the reduction of menthone oxime (Abstr., 1892, 723). A comparison of the two substances, and of some derivatives, shows that whilst the bases have almost identical boiling points, they and their derivatives have opposite and equal optical activities, the first being dextrorotatory, the second lævorotatory. The compound prepared from ammonium formate always contains a little lævorotatory menthylamine. The following table gives the melting points of the chief derivatives of these compounds; column I refers to Wallach's compound, column II to Andres and Andréeff's:—

	I.	II.
Menthylamine hydrogen chloride, $C_{10}H_{19}\cdot NH_2,HCl$	M. p. 189°	Unmelted at 280°
Formylmenthylamine, $C_{10}H_{19}\cdot NH\cdot COH$	„ 117—118°	M. p. 102°
Acetylmenthylamine, $C_{10}H_{19}\cdot NHAc$	„ 168°	„ 144°
Propionylmenthylamine, $C_{10}H_{19}\cdot NH\cdot COEt$	„ 151°	„ 89°
Butyrylmenthylamine, $C_{10}H_{19}\cdot NH\cdot COPr^{\alpha}$	„ 106°	„ 76—77°
Phenylmenthylthiocarbamide, $C_{10}H_{19}\cdot NH\cdot CS\cdot NHPh$	„ 178—179°	„ 135°

J. B. T.

Constituents of Oil of Thuja. By O. Wallach (*Annalen*, **272**, 99—122).—Thuja oil, which, according to Jahns (*Arch. Pharm.*, **221**, 748), consists principally of thujol, an isomeride of camphor, can be separated by distillation into three principal fractions boiling at 160—190°, 190—200°, and 200—215° respectively. The fraction of lowest boiling point contains pinene, probably also ethereal salts of acetic acid. The intermediate fraction, which forms the principal portion of the oil, consists of a mixture of levo-fenchone and thujone, which can be only partially separated by repeated fractional distillation. The fraction of highest boiling point has not yet been investigated.

Levo-fenchone, $C_{10}H_{16}O$, is easily obtained in a pure state by boiling the fraction distilling at 190—195° with concentrated nitric acid in order to oxidise the thujone, and then distilling the unchanged fenchone with steam. It melts at 5°, boils at 192—194°, and its sp. gr. is 0·948 at 20°; its specific rotatory power is $[\alpha]_D = -66·94°$, and its refraction $[n]_D = 1·46355$ or $M = 44·21$, the calculated value being $M = 44·11$; these properties show it to be the optical isomeride of the dextro-fenchone previously described (Abstr., 1891, 218 and 1086; 1892, 1237).

Levo-fenchyl alcohol, $C_{10}H_{17}\cdot OH$, prepared by reducing the ketone with sodium and alcohol, has a specific rotatory power $[\alpha]_D = 10{\cdot}36°$.

Levo-fenchone oxime, $C_{10}H_{16}{:}NOH$, the *nitrile*, $C_9H_{15}\cdot CN$, the *α-iso-oxime*, $C_{10}H_{17}NO$, the *β-iso-oxime*, *levo-fenchylamine*, and some of its derivatives, were prepared and found to be identical, except as regards the sign of their rotatory power, with the corresponding derivatives of dextro-fenchone (*loc. cit.*).

A number of the racemic modifications of the derivatives of fenchone were obtained by the combination of the two active modifications; in the following table, the melting points of the active and inactive compounds are given :—

	Active.	Inactive.		Active.	Inactive.
Fenchyl alcohol...	40°	33—35°	Benzylidenefenchylamine.....	42°	liquid
Fenchone oxime...	160—161	158—160	Hydroxybenzylidenefenchylamine	95	64—65°
α-Iso-oxime.....	114—115	98—99	Phenylfenchylthiocarbamide.....	152—153	169—170
β-Iso-oxime	137	160—161			

Thujone, $C_{10}H_{16}O$, boils at a higher temperature than fenchone, but it is doubtful whether it has yet been obtained free from the latter. It combines with hydroxylamine yielding an oily oxime, and, on reduction with sodium and alcohol, it is converted into an alcohol of the composition $C_{10}H_{18}O$, boiling at 210—212°.

Thujylamine is obtained, together with fenchylamine, when crude thujone is heated with ammonium formate and the product hydrolysed; it is purified by means of its hydrochloride, which is insoluble in ether, that of fenchylamine being soluble; it boils at 198—199°. The *hydrochloride*, $C_{10}H_{19}N,HCl$, and the *nitrate* are readily soluble in water, but the *sulphate* is only sparingly soluble; the *platinochloride* has the composition $(C_{10}H_{19}N)_2,H_2PtCl_6$. When the hydrochloride is submitted to dry distillation, it is decomposed into ammonium chloride and a hydrocarbon of the composition $C_{10}H_{16}$, which is named *thujene;* this compound boils at 172—175°, its sp. gr. is 0·840 at 20°, and its refractive power is $[n]_D = 1{\cdot}4761$.

α-Thujaketonic acid, $C_{10}H_{16}O_3$, or *β-thujaketonic acid*, $C_{10}H_{16}O_3$, is produced when thujone is oxidised with potassium permanganate, but the conditions which lead to the formation of one or the other compound have yet to be determined.

The *α*-acid crystallises from water in well-defined, transparent plates, melts at 75—76°, and is completely soluble in about 40 parts of boiling water; when heated, it is converted into a ketone with evolution of carbonic anhydride. The *silver* salt, $C_{10}H_{15}O_3Ag$, is only sparingly soluble in cold water. The *oxime*, $C_{10}H_{17}NO_3$, separates from alcohol and water in crystals, melts at about 168° with decomposition, and is only sparingly soluble in ether, and very sparingly in water.

The β-acid crystallises from boiling water in small needles, melts at 78—79°, and is completely soluble in about 70 parts of boiling water. The *silver* salt, $C_{10}H_{15}O_3Ag$, separates from boiling water, in which it is only very sparingly soluble, in crystals. The *oxime*, $C_9H_{17}NO_2$, melts at 104—106°, and separates from dilute alcohol in needles.

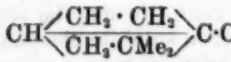
Methyl heptylene ketone, $C_9H_{16}O$, is formed, together with a smaller quantity of a liquid acid and carbonic anhydride, when β-thujaketonic acid is submitted to dry distillation. It boils at 184—186°, and is volatile with steam; its sp. gr. is 0·854 at 20°, and its refraction $[n]_D = 1·44104$. It combines directly with bromine, and yields an oxime on treatment with hydroxylamine; it is readily oxidised by potassium permanganate, and, on reduction with sodium and alcohol, it is converted into an alcohol which has an agreeable odour recalling that of linalol. When warmed with zinc chloride, it is converted into an unsaturated hydrocarbon of the composition C_9H_{14}, which yields solid nitro-derivatives on treatment with concentrated nitric acid. F. S. K.

Camphors containing the Group CO·CH$_3$. By F. W. Semmler (*Ber.*, **25**, 3343—3352).—*Tanacetone*, $C_{13}H_{16}O = C_9H_{13}·CO·CH_3$, is contained in the oils of tansy (*Tanacetum vulgare*), absinth, sage, and thuja, usually to the extent of about 50 per cent.; it may be separated by means of its crystalline sodium hydrogen sulphite compound or its oxime. It is an oil boiling at 84·5° under 13 mm. pressure, dissolves in ether but not in water, has a sp. gr. 0·9126 at 20°, its refractive power $[n]_D = 1·4495$, and its rotation is +38° 30′ in a column 200 mm. long. It appears to have the formula given at the end of this abstract. When reduced with sodium, it yields *tanacetyl alcohol*, $C_9H_{13}·CHMe·OH$, which boils at 92·5° under 13 mm. pressure, has a sp. gr. of 0·9249 at 20°, and a refractive power $[n]_D = 1·4635$. This substance behaves like a saturated compound, bromine forming substitution, and not additive derivatives; phosphoric chloride converts it into *tanacetyl chloride*, boiling at 72° under 10 mm. pressure. With hydroxylamine, tanacetone yields *tanacetoxime*, $C_9H_{13}·CMe:NOH$, which melts at 51·5° and boils at 135—136° under 20 mm. pressure. When reduced with sodium, the oxime yields *tanacetylamine*, $C_9H_{13}·CHMe·NH_2$, which boils at 80·5° under 14 mm. pressure, has a sp. gr. of 0·8743 at 20°, and a refractive power $[n]_D = 1·462$; it behaves like a fatty amine in taking up carbonic anhydride from the air. Its hydrochloride, $C_{10}H_{19}N,HCl$, is insoluble in ether; when distilled, it yields *tanacetene*, $C_{10}H_{16}$, which boils at 60—63° under 14 mm. pressure, has a sp. gr. of 0·8408 at 20°, and a refractive power $[n]_D = 1·476$; it appears to be a terpene with two ethylene linkings.

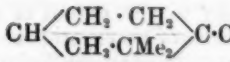
When tanacetone is shaken with alkaline hypobromite, bromoform is liberated (proof of CO·CH$_3$ group) and *tanacetogenic acid* formed. This is an oil which boils at 113·5° under 15 mm. pressure, and forms needles when placed in a freezing mixture; it behaves like a saturated compound; its *silver salt*, $C_9H_{13}O_2Ag$, is somewhat sensitive to light. If tanacetone is oxidised with permanganate, *tanacetoketocarboxylic*

acid is formed; this crystallises from light petroleum in needles melting at 78°, but from hot water usually in rhombohedral plates melting at 74·5°. These two varieties are probably geometrically isomeric, and are identical with the β- and α-thujaketonic acids of Wallach (preceding abstract). The *silver salt*, $C_{10}H_{15}O_3Ag$, forms a white precipitate; the *oxime*, $C_{10}H_{16}O_2{:}NOH$, exists in two varieties, α- melting at 168·5° and β- at 103°, prepared respectively from the acids melting at 74·5° and 78°. If the acid itself is dissolved in soda and bromine added, bromoform and *tanacetogendicarboxylic acid* are formed. This acid melts at 141·5°, but a geometrically isomeric variety, melting at a much lower temperature, appears also to exist. It yields a *silver salt*, $C_9H_{12}O_4Ag_2$, and, like all orthodicarboxylic acids, an anhydride when heated with acetic anhydride. This *anhydride*, $C_9H_{12}O_3$, forms white needles, melts at 55°, and boils at 171·5° under 16 mm. pressure. When the acid is fused with potash, pimelic acid is formed, but if distilled with soda-lime, it yields *tanacetophorone*, $C_9H_{12}O$, an oil with an odour like that of camphorone. This boils at 89—90° under 13 mm. pressure, and has a refractive power $[n]_D = 1{\cdot}4817$; it appears to be a ketone.

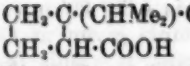
The formulæ assigned to the above-mentioned compounds are as follows:—



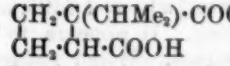
Tanacetone.



Tanacetogenic acid.



Tanacetoketocarboxylic acid.



Tanacetogendicarboxylic acid.

C. F. B.

Campholamine. By G. Errera (*Gazzetta*, **22**, ii, 109—122; compare Abstr., 1892, 1345).—*Campholamine*, $C_{10}H_{19}{\cdot}NH_2$, is prepared by saturating a boiling solution of campholonitrile in absolute alcohol with sodium, adding water, acidifying the solution with hydrochloric acid, and distilling in a current of steam to eliminate any unchanged nitrile. On rendering the solution alkaline with soda, and again distilling in a current of steam, the pure amine is obtained as a colourless oil lighter than water. It has an alliaceous, ammoniacal odour, and boils at 210°, but is readily volatile at ordinary temperatures. It absorbs carbonic anhydride from the air, forming a white, crystalline substance, which is probably *campholyl camphocarbamate*, $C_{10}H_{19}{\cdot}NH{\cdot}CO{\cdot}NH_2(OH){\cdot}C_{10}H_{19}$. The amine is insoluble in alkalis, and sparingly soluble in water. The *hydrochloride*, $C_{10}H_{19}{\cdot}NH_2,HCl$, crystallises in colourless, silvery laminæ, soluble in water, and decomposes on heating. The *platinochloride*,

$$(C_{10}H_{19}{\cdot}NH_2)_2,H_2PtCl_6,$$

separates from alcohol in beautiful yellow laminæ. The *nitrate* is sparingly soluble in cold water, and forms silvery scales; it melts

with decomposition at 210° or 220°, according as the heating is slow or rapid. The *benzoyl* derivative crystallises from light petroleum in lustrous, colourless needles, melting at 98°.

Phenylcampholylthiocarbamide, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_{10}H_{19}$, is obtained by the interaction of ethereal solutions of campholamine and phenylthiocarbimide in molecular proportion. The carbamide separates immediately, and crystallises from dilute alcohol in colourless needles melting at 117—118°; it is very soluble in alcohol, sparingly so in light petroleum, and insoluble in water.

Campholylcamphelylcarbamide, $C_{10}H_{17}{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_9H_{17}$, is obtained by the action of campholamine on camphelylthiocarbimide in ethereal solution. It separates from dilute alcohol in lustrous, colourless needles melting at 259—260°; it is very soluble in alcohol, sparingly so in ether, and insoluble in water.

On mixing hot aqueous solutions of silver nitrite and campholamine hydrochloride in molecular proportion, campholamine nitrite is formed, and on prolonged boiling with water, decomposes with evolution of nitrogen, and formation of an oil, which distils with the steam. The oil, after washing with dilute hydrochloric acid, is dried, and on fractional distillation yields two products, boiling at 160—165° and 200—205° respectively. The former, *campholene*, $C_{10}H_{18}$, is a mobile, colourless liquid of pleasant odour, which immediately reduces permanganate or bromine water. It boils at 163°, and is possibly identical with the hydrocarbon obtained by Weyl (*Ber.*, **1**, 96) by heating camphor with hydriodic acid. The substance boiling at the higher temperature is *campholyl alcohol*, $C_{10}H_{19}{\cdot}OH$; it is a colourless, slightly oily liquid, of pleasant, aromatic odour, and boils at 203°.

The author terms the hydrocarbon $C_{10}H_{18}$ *campholene*, identifying it with the campholic series; its lower homologue, C_9H_{16}, which is ordinarily termed campholene, the author prefers to call *camphelene*. The constitutional formulæ involved in the above reactions are discussed, but no definite result is arrived at.

Campholenamide is optically active, and melts at 127—128°. In 3—9 per cent. solutions $[\alpha]_D = -3{\cdot}8°$ approximately.

W. J. P.

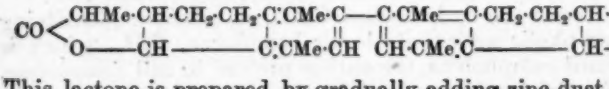
Derivatives of Amethylcamphonitroketone. By P. Cazeneuve (*Bull. Soc. Chim.* [3], **7**, 327—331; compare Abstr., 1892, 999 and 1085).—The *sodium* derivative of amethylcamphonitroketone, $NO_2{\cdot}C_9H_{14}NaO + 2H_2O$, forms red, micaceous scales, is soluble in water and in alcohol, and deflagrates on heating. The *ethyl* derivative, $NO_2{\cdot}C_9H_{13}EtO$, obtained by heating the potassium compound with excess of ethyl iodide in a sealed tube at 130°, is a syrupy liquid not miscible with water, but soluble in alcohol and ether; when treated with sodium ethoxide, it decomposes into ethyl ether and the sodium derivative of the nitro-ketone, but if dissolved in toluene and heated with sodium, it is converted into an amorphous *compound* $NO_2{\cdot}C_9H_9NaEtO$. The *acetyl* derivative, $NO_2{\cdot}C_9H_{13}AcO$, is obtained by adding acetic chloride to the anhydrous sodium or potassium derivative, or by heating them with acetic anhydride at 150°; the product is triturated with cold alkali and crystallised from alcohol; it forms six-sided tables, melts at 65°, explodes at 250°, and decom-

poses into ethyl acetate and the sodium derivative of the nitro-ketone on treatment with sodium ethoxide. When the acetyl derivative is dissolved in toluene and treated with sodium, the compound $NO_2 \cdot C_9H_9NaAcO$ is formed; it has the colour of mercuric iodide, dissolves in water, but is gradually decomposed by it, and is more soluble in alcohol. A compound soluble in alkalis is also formed in this reaction; it is perhaps a pinacone. A. R. L.

Tinctorial Properties of Amethylcamphonitroketone. By P. Cazeneuve (*Bull. Soc. Chim.* [3], **7**, 331—332).—Amethylcamphonitroketone (preceding abstract) dyes wool or silk without a mordant, not, however, in an alkaline bath; cotton mordanted with tannin also fixes the compound. The compound contains the chromophoric group NO_2, but no salt-forming (auxochromic) group. The group CH_2 is of an acidic nature by virtue of its position between the groups NO_2 and CO (see Abstr., 1892, 1085), and the tinctorial properties of the nitroketone are, perhaps, to be ascribed to this circumstance. A. R. L.

Coniferin. By E. O. v. Lippmann (*Ber.*, **25**, 3220—3221).—The author has isolated coniferin from *Scorzonera hispanica*. Vanillin appeared also to be present in small quantities, but could not be separated from other aldehydic substances present. L. T. T.

Reduction Products of the Santonins, Santonone, and Isosantonone. By G. Grassi-Cristaldi (*Gazzetta*, **22**, ii, 123—129; compare Abstr., 1892, 869).—*Santonone*,



This lactone is prepared by gradually adding zinc-dust (5—6 grams) to a hot solution (300 c.c.) of santonin (10 grams) in acetic acid (50 per cent.), preferably in presence of a little platinum tetrachloride. After six hours' heating, the crystalline deposit is collected, washed with water, dried, and extracted with boiling alcohol in a reflux apparatus. Santonone separates from the alcoholic solution on cooling. It forms silky, white needles melting at 223°; it is very soluble in benzene, less so in hot alcohol, ether, or dilute acetic acid, and insoluble in water. It is optically active in solution; for a 2 per cent. solution in benzene $[\alpha]_D = +129{\cdot}46°$; its molecular weight, as determined by the cryoscopic or the boiling-point method in benzene solution, is normal.

Santononic acid, $C_{30}H_{38}O_6$, is a bibasic acid, obtained by boiling a solution of santonone in dilute barium hydroxide for 10 hours. After precipitating the excess of barium by carbonic anhydride, and filtering, the acid is precipitated by acetic acid, collected, washed, dissolved in absolute alcohol, and allowed to crystallise. It is thus obtained in beautiful, micaceous laminæ melting at 215—216° with decomposition. It is very soluble in ethyl or methyl alcohol, sparingly so in ether, benzene, ethyl acetate, or chloroform, and insoluble in water. In a 1 per cent. alcoholic solution, it has the specific

rotatory power $[\alpha]_D = +37{\cdot}08°$ at 20°. The aqueous solution of its ammonium salt gives white precipitates with zinc, mercuric, lead, or cadmium salts; precipitates are produced on heating with manganese, nickel, or cobalt salts. Copper sulphate gives a blue precipitate. On dehydration with acetic anhydride, the acid yields santonone.

Isosantonone, $C_{30}H_{34}O_4$, an isomeride of santonone, is obtained by slowly adding concentrated sulphuric acid to a cooled, concentrated alcoholic solution of santononic acid. It is a white substance melting with decomposition at 280°; it is very soluble in chloroform, sparingly in ethyl acetate, acetic acid, ether, ethyl or methyl alcohol, and benzene, and insoluble in water or light petroleum. It gives a normal molecular weight by the cryoscopic method in acetic acid solution, and in a 1 per cent. glacial acetic acid solution has the specific rotatory power $[\alpha]_D = -264{\cdot}7°$. It is also formed on heating a solution of santononic acid in dilute alcohol, water, or ether on the water-bath. The glacial acetic acid solution of santononic acid is lævorotatory owing to partial conversion into santonone; the lævorotation gradually increases. Isosantonone may be also prepared by slowly adding zinc-dust to a heated solution of santonin (10 grams) in 70 per cent. acetic acid (300 c.c.); a little platinum tetrachloride is also added. After six hours' heating on the water-bath, the isosantonone is precipitated from the solution by water.

Isosantononic acid, $C_{30}H_{38}O_6$, an isomeride of santononic acid, is prepared from isosantonone in the same way as santononic acid is obtained from santonone. It is a white powder which melts at 167—168°. On heating at 200°, it is reconverted into isosantonone; the same change occurs slowly at 100°. It is optically active in solution; in a 1 per cent. alcoholic solution $[\alpha]_D = -40{\cdot}39°$. Solutions of its salts are very unstable, decomposing with separation of the lactone; the *silver* salt, $C_{30}H_{36}O_6Ag_2$, is a white, granular powder.

There is a very marked analogy in properties, indicating constitutional similarities, between the hyposantonines and the santonones.

W. J. P.

Santonin. By J. Klein (*Arch. Pharm.*, **230**, 499—513).—Constitutional formulæ for santonin have been proposed by Cannizzaro (Abstr., 1886, 73), and recently by Grassi-Cristaldi (*Ber.*, **24**, Ref. 908), which represent it as a hydrogenised naphthalene derivative. The author points out, however, that in the production of naphthalene derivatives from santonin, three carbon atoms are invariably removed, which may exist in the compound as an isopropyl group. Taking into account this possibility, together with the fact that cineol occurs in wormseed together with santonin, it seems not improbable that santonin may be related to the terpenes, and be a derivative of a *hydrocarbon*, $\begin{matrix}CH_2\cdot CMe\cdot CH\cdot CH_2\cdot CH_2\\ CH_2\cdot CMe\cdot CH\cdot CH_2\cdot CH\cdot CHMe_2\end{matrix}$, which may be named *santogenene*. Santoninic acid would then be *ketohydroxysantogenenic acid* and santonin *ketohydroxysantogenenic lactone*.

Dihydroxysantogenenic acid, $OH\cdot C_{12}H_{18}(CH\cdot OH)\cdot COOH$, is obtained by the action of sodium on an alcoholic solution of santonin; it forms white, pointed crystals, melts at 162—164°, and is readily soluble in

alcohol and ether. The *silver* salt is a white, crystalline precipitate which blackens on warming with water.

Hydroxysantogenenic acid, $OH{\cdot}C_{13}H_{18}(CH_2){\cdot}COOH$, is formed when santonin is heated with hydriodic acid and amorphous phosphorus; it crystallises from dilute alcohol in delicate needles, melts at 174°, and is readily soluble in ether, alcohol, and benzene. The *silver* salt is a white, amorphous precipitate, which is reduced on boiling with water. Cannizzaro and Carnelutti obtained an acid (m. p. 178—179°) in the above given manner, to which they erroneously ascribed the formula $C_{15}H_{20}O_3$, this acid being, doubtless, identical with that just described.

When santonin is dissolved in a mixture of glacial acetic acid and alcohol, and an excess of zinc-dust gradually added to the hot solution, a *dilactone*, $C_{30}H_{36}O_4$, separates from the filtrate on adding water, whilst a compound resembling santonin, but melting at 163—164°, is isolated on evaporating the mother liquor. The dilactone crystallises from alcohol in yellowish-green needles, melts at 200—201°, and when dissolved in alcoholic alkali, the solution evaporated, and the residue redissolved in water and hydrochloric acid added, an isomeride more sparingly soluble in alcohol and crystallising therefrom in small, white needles is obtained; this melts at 260—261° forming a dark liquid. The compounds are provisionally distinguished as α- and β-santogenenic dilactone. A. R. L.

Santonin. By J. Klein (*Ber.*, **25**, 3317—3318).—When bromine and santonin are dissolved in molecular proportion in glacial acetic acid, and the solution, after remaining for some hours, is poured into water, an additive compound, $C_{15}H_{18}O_3,C_2H_4O_2,Br_2$, is precipitated; when crystallised from alcohol, it melts a little above 60°, decomposes on exposure to light, but is stable when kept in the dark. Santonin is regenerated when the additive compound is boiled with aqueous alcoholic potash; whilst *bromosantonin*, $C_{15}H_{17}BrO_3$, is obtained when it is boiled with alcohol. The latter crystallises from alcohol in leaflets, melts at 149—151°, and its behaviour towards nitric acid indicates that the bromine is contained in the aromatic nucleus. Santonin, when dissolved in alcohol or ether and treated with hydrogen chloride, does not form an additive compound, but when treated with phosphoric chloride (2 mols.), it yields a *chloride*, $C_{15}H_{16}Cl_2O$, which seems by its behaviour towards nitric acid to contain the chlorine in the side-chain. A. R. L.

Cephalanthin. By C. Mohrberg (*Chem. Centr.*, 1892, ii, 363; from *Arb. Pharm. Inst. Dorpat*, **8**, 20—50; compare Claasen, Abstr., 1890, 171).—By extracting cephalanthus bark with boiling water and fractionally precipitating the extract with lead acetate, in three fractions, there were obtained in the first cephalanthin and colouring matters, in the second a tannin, and in the third a saponin. But the greater portion of the cephalanthin is contained in the pressed bark, and is obtained by boiling this with lime water, precipitating the lime with carbonic anhydride, and, finally, the cephalanthin with hydrochloric acid. It is very bitter, even in dilution of 1 : 15,000,

very soluble in alcohol, ethyl acetate, ammonia, and soda, slightly in hot and cold water, ether, and chloroform, not at all in benzene and light petroleum. It is a feeble acid, and displaces carbonic anhydride from carbonates. Its composition is $C_{22}H_{34}O_6$; it begins to liquefy at 177°, and melts at 180·1° (corr.), and in alkaline solution has $[\alpha]_D = 20·25°$. Strong sulphuric acid colours it orange, hydrochloric acid violet, sulphovanadic acid pink, dilute gallic acid or strong sulphuric at 70° at first red, then violet, α-naphtholsulphonic and thymolsulphonic acids violet or reddish-violet. Acids decompose it into a sugar, $C_6H_{12}O_6$ (whose phenylosazone melts at 196—198°), and an acid substance, *cephalanteïn*, $C_{16}H_{22}O_3$; it is thus a glucoside.

The cephalanthus tannin mentioned above is a reddish-yellow powder, soluble in alcohol and hot water, and gives a green coloration with ferric salts. It is probably a mixture of "true tannic acid" with another substance, the cephalethin of Claasen. The cephalanthus saponin is a poison which dissolves the blood corpuscles; it is not very active, however.

Cephalanthin, when injected, acts as a poison, dissolving the blood corpuscles, the colouring matter of which goes into the serum and the urine as oxyhæmoglobin, and is then changed into methæmoglobin. Cramp, vomiting, and paralysis appear, and jaundice, caused by an enormously increased secretion of bile. Among the earlier symptoms are movements of the intestines, but neither the heart, vagus nerve, nor vasomotor system is affected. The iron separated out in the liver gets into the spleen, lymphatic glands, and marrow, and is used up in the formation of blood; a part goes into the kidneys.

C. F. B.

Identity of Cascarin and Rhamnoxanthin. By T. L. Phipson (*Compt. rend.*, **115**, 474).—The cascarin obtained by Leprince (Abstr., 1892, 1483) from *Cascara sagrada* (*Rhamnus prushiana*) is identical with the rhamnoxanthin obtained by the author in 1858 from the bark of *Rhamnus frangula*.

C. H. B.

Action of Hydrogen Peroxide on Piperidine Bases. By G. Merling (*Ber.*, **25**, 3123—3127).—Hydroxy-bases are obtained from tropidine, tropine, hydrotropidine, and methyl-α- and -β-pipecoline by allowing these compounds to remain with 15 parts of commercial hydrogen peroxide at the ordinary temperature for some days. The hydroxy-bases are colourless, crystalline compounds, are very hygroscopic, cannot be distilled without decomposition, and have a faint alkaline reaction. They are unaltered when heated with concentrated hydrochloric acid at 140—170°. The action of hydrochloric acid on hydroxytropine has not been examined. Hydroxyhydrotropidine, $C_8NH_{15}O$, obtained from hydrotropidine, is not identical with tropine or with Liebermann's pseudotropine, and therefore the author concludes that the oxygen atom is not attached to a β- or γ-methylene group. The author believes that these hydroxymethylpiperidine bases contain the complex $HO·CH_2·N<$, since they do not lose water when heated with concentrated hydrochloric acid, and secondary piperidine bases are not hydroxylated when treated with hydrogen peroxide. Hydr-

oxytropidine and hydroxymethylpiperidine, when warmed with concentrated hydriodic acid and then treated with sulphurous acid yield trop dine and methylpiperidine respectively.

α-Methyltropidine, C_9NH_{15}, is converted by hydrogen peroxide into the compound $C_9NH_{15}O$. The latter is very unstable, and decomposes when warmed in aqueous solution, probably yielding dihydrobenzaldehyde and dimethylamine.

The above hydroxy-bases were characterised by means of the platinochlorides.

Hydroxytropidine platinochloride, $(C_7NH_{10}\cdot CH_2\cdot OH)_2.H_2PtCl_6$, crystallises from water in large, lustrous, orange-yellow plates, melts at 220° with decomposition, and is sparingly soluble.

Hydroxytropine platinochloride, $(C_7NH_{12}O\cdot CH_2\cdot OH)_2,H_2PtCl_6,2H_2O$, crystallises in orange-yellow tablets, is easily soluble, and effloresces on exposure to air.

Hydroxyhydrotropidine platinochloride, $(C_7NH_{12}\cdot CH_2\cdot OH)_2,H_2PtCl_6$, crystallises in lustrous, orange-yellow prisms, melts at 228° with decomposition, and is easily soluble.

Hydroxymethyl-α-pipecoline platinochloride,

$$(C_6NH_{12}\cdot CH_2\cdot OH)_2,H_2PtCl_6,2H_2O,$$

crystallises from hot water in orange crystals, when dry melts at 202° with decomposition, and is very sparingly soluble in cold water.

Hydroxymethyl-β-pipecoline platinochloride,

$$(C_6NH_{12}\cdot CH_2\cdot OH)_2,H_2PtCl_6,$$

crystallises in orange-red prisms, melts at 196—197° with decomposition, and is easily soluble.

Hydroxymethylpiperidine platinochloride,

$$(C_5NH_{10}\cdot CH_2\cdot OH)_2,H_2PtCl_6,2H_2O,$$

crystallises in beautiful, orange-red prisms, when dry it melts at 194° with decomposition, and is sparingly soluble.

Hydroxydihydrobenzyldimethylamine platinochloride,

$$(C_9NH_{13}O)_2,H_2PtCl_6,$$

is obtained in yellow leaflets which are sparingly soluble, and blacken when heated with water. E. C. R.

Non-nitrogenous Acids derived from Pyridinecarboxylic acids. By H. Weidel and J. Hoff (*Monatsh.*, **13**, 578—602; compare Abstr., 1891, 733, 1525).—Cinchonic acid, which, as has been previously shown, is formed by the action of sodium amalgam on cinchomeronic acid, $C_7H_5NO_4$, behaves generally in the same way as a bibasic acid, and, on saturation with carbonates, yields secondary salts, of the formula $C_7H_6M_2O_6$, which, however, are converted by hydroxides into tertiary salts, $C_7H_7M_3O_7$. On ethylation, cinchonic acid gives a compound containing two ethyl groups, $C_7H_8O_6Et_2$, and this is converted by phosphorus pentachloride into an unstable chloro-compound, which, on treatment with alcohol, yields the triethyl salt of the tricarboxylic acid, $C_4H_7Cl(COOH)_3$.

On reduction with hydriodic acid, cinchonic acid forms the tricarboxylic acid, $C_7H_{10}O_6$, which was obtained by the authors in the form of two stereo-isomeric modifications. When this acid is heated, carbonic anhydride escapes, and α-methylglutaric acid is formed.

On dry distillation, cinchonic acid loses water and carbonic anhydride, and forms pyrocinchonic anhydride, $C_6H_6O_2$, which readily combines with nascent hydrogen, and is converted thereby into dimethylsuccinic acid. When digested with sodium ethoxide, cinchonic acid forms δ-hydroxyethylsuccinic acid, which, on reduction, yields ethylsuccinic acid. The behaviour of cinchonic acid characterises it as a lactonic acid, and points to its being δ-hydroxy-$\alpha\beta\gamma$-butenyltricarboxylic acid; moreover, the decomposition with nascent hydrogen from sodium amalgam takes place in a manner perfectly analogous to that observed in the reduction of pyridinecarboxylic acid, in which case the formation of the CO group in the α-position is also observed.

G. T. M.

Some Ammonium Compounds. By H. Decker (*Ber.*, **25**, 3326—3328).—The formation of quinolone derivatives (Abstr., 1892, 729) proceeds without the addition of potassium ferricyanide when concentrated solutions of quinoline alkyl iodides are distilled with steam in the presence of alkali; the quinolones are dissolved in the aqueous distillate, but an oil, consisting of alkyldihydroquinoline, also passes over. The author considers it not improbable that an ammonium hydroxide, $\begin{matrix}CH\cdot C_6H_4\\ \|\\ CH-CH\end{matrix}\!\!>\!NR\cdot OH$, is initially formed, which changes into a hydroxydihydroquinoline, $\begin{matrix}CH-\!\!-C_6H_4\\ \|\\ CH\cdot CH(OH)\end{matrix}\!\!>\!NR$, and then decomposes into the above-mentioned oxidation and reduction products.

A. R. L.

Bases from Polei Oil. By O. Wallach (*Annalen*, **272**, 122—125; compare Beckmann and Pleissner, Abstr., 1891, 936).—Two bases are formed when oil of polei, from *Mentha pulegium*, is heated with ammonium formate. The one boils below 170°, and its salts are readily soluble; its *hydrochloride*, $C_7H_{15}N,HCl$, melts at 174—176°, and distils at a higher temperature without appreciable decomposition; its *platinochloride*, $(C_7H_{15}N)_2,H_2PtCl_6$, separates from hot water in crystals.

The other base boils at about 250°, and its salts are comparatively sparingly soluble; its *hydrochloride* crystallises well, and has the composition $C_{14}H_{27}N.HCl$ or $C_{15}H_{29}N,HCl$; its *nitrate* is almost insoluble in cold water; its *platinochloride* is crystalline but unstable.

When the liquid pulegone oxime is reduced with sodium and alcohol, it is converted into a base which is quite different from either of the two compounds mentioned above, but which has certain points of similarity with fenchylamine and menthylamine; the crystalline pulegone oxime shows quite a different behaviour.

F. S. K.

Quinine Double Salts. By E. Grimaux (*Compt. rend.*, **115**, 608—610).—The author has previously adduced evidence in support

of the view that, in basic quinine salts, the acid is not united to the nitrogen of the quinoline group, but to another group, probably of the character of piperidine. If this hypothesis is correct, the quinoline group should be able to unite with another acid and produce double salts.

When 30 parts of crystallised basic quinine sulphate (1 mol.) is dissolved in 24·9 c.c. of hydrochloric acid of the sp. gr. 1·050 (2 mols.), and the solution is allowed to evaporate spontaneously in dry air, the salt, $(C_{20}H_{22}N_2O_2)_2,2HCl,H_2SO_4 + 3H_2O$, is obtained in acicular crystals, which lose 3 mols. H_2O at 100°. One part of the anhydrous salt dissolves in 1·16 parts of water at 25°. The hydrated salt melts at 120°, and the anhydrous salt melts, indistinctly, with some decomposition, at 165—170°. If only half the quantity of hydrochloric acid is used, solution takes place much less easily, and the hot liquid, when cooled, deposits basic quinine sulphate. On further evaporation, it yields the hydrochlorosulphate.

Quinine hydrobromosulphate, $(C_{20}H_{22}N_2O_2)_2,2HBr,H_2SO_4 + 3H_2O$, is obtained in a similar manner, by dissolving the basic sulphate (1 mol.) in hydrobromic acid (2 mols.). It forms a hard, white mass of small needles, loses 3 mols. H_2O at 100°, and is less soluble than the chlorine compound.

The hydriodosulphate is obtained in a similar manner, and forms yellowish crystals, which lose water in a dry vacuum or at 100°, and become brown, but absorb water and regain their yellow colour when exposed to the air.

Phosphoric acid yields analogous double salts. The chlorine compound has the composition $(C_{20}H_{22}N_2O_2)_2,2HCl,H_3PO_4 + 9H_2O$. They all crystallise in needles, the bromide with 7 mols. H_2O, and the iodide with 6 mols. H_2O. C. H. B.

Hydrastine. By M. Freund (*Annalen*, **271**, 311—408).—In this paper, the author gives, in a connected manner, the results of the investigations by which the constitution of hydrastine has been determined, and also briefly describes the more important decomposition products of the alkaloïd; most of the work has already been published (compare Abstr., 1890, 53, 534; 1891, 92, 93, 1578), but the following results are communicated for the first time:—Two isomerides of the composition $C_{10}H_9NO_4$ are produced when hydrastine is oxidised with potassium permanganate at about 40° (compare Abstr., 1889, 627 and 1220); the two componnds are more easily prepared by heating hydrastinic acid, $C_{11}H_9NO_6$, at 170° for a few minutes, and are separated with the aid of boiling alcohol. The one is deposited from the hot alcoholic extract in yellowish crystals, melts at 211—212°, and is readily soluble in hot water, alcohol, and glacial acetic acid, but insoluble in benzene, ether, carbon bisulphide, and chloroform; it can also be obtained by heating methylamine hydrastinate at 180°. The isomeride is insoluble in boiling alcohol, benzene, and chloroform, and only sparingly in water and glacial acetic acid; it separates from concentrated hydrochloric acid in crystals, melts at 280°, and, like the compound just described, dissolves in concentrated sulphuric acid with a blue coloration.

Hydrastic acid methylimide, $C_{10}H_7NO_4$, prepared by boiling hydrastinic acid with dilute nitric acid, melts at 227—228°, not at 233° as previously stated (Abstr., 1889, 1220).

Hydrastic acid, $C_9H_8O_6$, crystallises from hot water in lustrous, hexagonal prisms, or in long, broad needles, and is almost insoluble in chloroform and light petroleum, and only very sparingly soluble in toluene, but more readily in ether, acetone, and ethyl acetate, and very readily in alcohol; when very slowly heated, it sinters at 171—172° and melts at 173·5—174° with effervescence, but when very quickly heated, the temperature can be raised to 185—187° before the acid melts and passes into the anhydride (see below). The *barium* salt, $C_9H_4O_6Ba + H_2O$, separates from hot water in plates. The *silver* salt, $C_9H_4O_6Ag_2$, is a colourless compound, almost insoluble in water; the *silver hydrogen* salt, $C_9H_5O_6Ag$, prepared from the ammonium hydrogen salt, crystallises in microscopic needles, and is sparingly soluble in hot water. The *copper* salt, $C_9H_4O_6Cu$, crystallises in small, dark green plates or prisms; the *copper hydrogen* salt, $(C_9H_5O_6)_2Cu + 6H_2O$, crystallises in light blue needles. The *ammonium hydrogen* salt, $C_9H_5O_6{\cdot}NH_4$, crystallises from hot water in lustrous needles, sinters at 209—212°, and melts at 245—250° with decomposition. The methylamine salt, $C_9H_6O_6,NH_2Me$, is formed when hydrastic acid methylimide is boiled with 33 per cent. potash until the solution begins to become turbid (compare Abstr., 1889, 1220); it crystallises from hot water, melts at 225—226°, and is practically insoluble in most organic solvents. The *dimethyl* salt, $C_9H_4O_6Me_2$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from alcohol in colourless plates, and melts at 88—89°; the *methyl hydrogen* salt, $C_9H_5O_6Me$, melts at 136°, and is soluble in hot water, ether, and alcohol. The *anhydride*, $C_9H_4O_5$, crystallises from alcohol in needles, melts at 175°, and is only sparingly soluble in alcohol; it gives the fluoresceïn reaction.

Hydrastimide, $C_9H_5O_4N$, is formed when the ammonium hydrogen salt is heated for some time at its melting point; it crystallises from glacial acetic acid in colourless, iridescent plates, sinters at 270°, melts at 275—277°, and is moderately easily soluble in acetone, but more sparingly in chloroform and water; its solutions show a slight fluorescence.

Dichlorhydrastic chloride, $CCl_2<^{O}_{O}>C_6H_2(COCl)_2$, is formed when hydrastic acid is heated at 175—185° with phosphorus pentachloride; it is an oil, and is gradually decomposed by water, being converted into a crystalline compound, which melts at 142—144°, and is, doubtless, *dichlorhydrastic acid*.

Normetahemipinic acid, $C_8H_6O_6 + H_2O$, is obtained when dichlorhydrastic acid is heated with water; it sinters at 190° and melts at 248°, being converted into the anhydride; it is identical with the acid described by Rossin (Abstr., 1892, 180), as is proved by crystallographic measurements and by the properties of its anhydride and ethyl hydrogen salt.

Benzoylhydrastinine, $C_{11}H_{12}NO_3Bz$, prepared by shaking hydrastinine

with soda and benzoic chloride, crystallises from dilute alcohol, and melts at 98—99°; its *oxime*, $C_{11}H_{12}NO_2Bz{:}NOH$, melts at 146°.

Benzoylhydroxyhydrastinine hydrate, $C_{11}H_{12}NO_4Bz + H_2O$, is formed when benzoylhydrastinine is oxidised with potassium permanganate in presence of alkali; it crystallises from dilute alcohol in prisms, loses its water at 105°, melts at 169—170°, and dissolves freely in alkalis.

Acetylhydrastinine, $C_{11}H_{12}NO_2Ac$, is obtained when hydrastinine is warmed with acetic anhydride in benzene solution; it crystallises from hot water in concentrically grouped needles, melts at 105°, and forms a crystalline hydrochloride which is decomposed by water.

Acetylmethylamidohydrastyleneacetic acid,

$$NMeAc{\cdot}C_{10}H_9O_2{:}CH{\cdot}COOH,$$

is formed when hydrastinine is boiled with acetic anhydride for two hours; it separates from hot acetic acid in crystals, melts at 219°, and is almost insoluble in cold water and ether, but soluble in alcohol, benzene, and chloroform. The compound obtained by treating hydrastinine with propionic anhydride in like manner melts at 135°. The *bromo*-derivative, $C_{15}H_{16}BrNO_5$, prepared by treating acetylmethylamidohydrastyleneacetic acid with bromine in chloroform solution, crystallises from hot dilute alcohol in colourless needles, and melts at 180—181°. The *barium* salt, $(C_{15}H_{16}NO_5)_2Ba$, is crystalline. The *methyl* salt, $C_{15}H_{16}NO_5Me$, crystallises from hot water in needles, and melts at 147°.

Phenylmethylhydrastylthiocarbamide, $C_{18}H_{18}N_2O_3S$, is obtained when hydrastinine is treated with phenylthiocarbimide in alcoholic solution; it separates from alcohol in almost colourless needles melting at 126°.

Methylhydrasteïneoxime anhydride, $C_{22}H_{24}N_2O_6$, can be prepared by boiling methylhydrasteïne with hydroxylamine hydrochloride in moderately concentrated aqueous solution; it crystallises from alcohol in lustrous, hexagonal plates, containing 1 mol. C_2H_6O, which is expelled at 80—85°; it melts at 158° and is almost insoluble in water and cold alcohol, but readily in hot alcohol. The *hydrochloride*, $C_{22}H_{24}N_2O_6,HCl + 3H_2O$, prepared by adding hydrochloric acid to an alcoholic solution of the base, crystallises from water in small, quadratic plates, and melts at 221°; the anhydrous salt is obtained in microscopic crystals when hydrogen chloride is passed into an alcoholic solution of the base. The *nitrate*, $C_{22}H_{24}N_2O_6,HNO_3$, crystallises from boiling alcohol in small prisms. The *sulphate*, $C_{22}H_{24}N_2O_6,H_2SO_4 + C_2H_6O$, crystallises from alcohol in lustrous, hexagonal plates, sinters at 80°, melts at 90°, and begins to decompose at 110°. The *methiodide*, $C_{22}H_{24}N_2O_6,MeI + 2H_2O$, crystallises from water in compact, yellowish prisms, loses its water at 125—130°, and melts at 155—156°; when boiled with potash, it is decomposed with evolution of trimethylamine, yielding a compound which crystallises from alcohol in yellow, hexagonal prisms, melts at 184—185°, and has the composition $C_{20}H_{17}NO_6$.

Methylhydrasteïnephenylhydrazone anhydride, $C_{28}H_{29}N_3O_5$, is formed when methylhydrasteïne is boiled with an alcoholic solution of

phenylhydrazine hydrochloride; it crystallises from alcohol in yellowish, quadratic prisms, melts at 175—176°, and is insoluble in water and only sparingly soluble in boiling alcohol. The *hydrochloride*, $C_{28}H_{29}N_3O_5,HCl$, crystallises in slender needles, and melts at 220—222°. The *nitrate*, $C_{28}H_{29}N_3O_5,HNO_3$, melts at 203—204°, and separates from hot alcohol in crystals. The *methiodide*,

$$C_{28}H_{29}N_3O_5,MeI,$$

is a transparent, highly-refractive, crystalline compound melting at 243°, and moderately easily soluble in hot dilute alcohol; when boiled with concentrated potash, it is decomposed with evolution of methylamine, being converted into a pale yellow, crystalline compound, which melts at 162—164°, and has the composition $C_{26}H_{23}N_3O_5$.

Nitromethylhydrastimide, $C_{22}H_{23}N_3O_7$, is obtained, together with dihydroxymethylhydrastimide, hemipinimide, and other compounds, when methylhydrastimide (compare Freund and Heim, Abstr., 1891, 92) is warmed with a mixture of equal parts of nitric acid of sp. gr. 1·15 and water, until the methylhydrastimide nitrate, which separates from the solution at first, has redissolved; the solution is then immediately cooled. The nitro-compound separates from hot alcohol in lustrous, red crystals, which contain 1 mol. C_2H_6O; these crystals sinter at about 85°, melt at about 95°, and then solidify, melting again at 138° to a dark red liquid which is completely decomposed at 170°; it also crystallises with benzene and with chloroform. Its salts crystallise well, and, with the exception of the nitrate, are all readily soluble in boiling alcohol and in hot water. The *hydrochloride*, $C_{22}H_{23}N_3O_7,HCl$, prepared by passing hydrogen chloride into a hot alcoholic solution of the base, crystallises in lustrous, yellow needles, and melts at 202—203°. The *nitrate*, $C_{22}H_{23}N_3O_7,HNO_3$, separates from dilute alcohol in crystals melting at 212°. The *sulphate*, $(C_{22}H_{23}N_3O_7)_2,H_2SO_4$, crystallises in yellow, microscopic needles, and melts at 195—196°; the *acid sulphate*, $C_{22}H_{23}N_3O_7,H_2SO_4$, forms golden needles, and melts at 250°. The *methiodide*, $C_{22}H_{23}N_3O_7,MeI$, crystallises from hot alcohol in orange plates, and decomposes at about 250°, but without melting.

Dihydroxymethylhydrastimide, $C_{21}H_{24}N_2O_7$, crystallises from hot alcohol in colourless needles, melts at 151°, and is soluble in acids and alkalis; when heated with dilute nitric acid, it is converted into hemipinimide. The *platinochloride*, $(C_{21}H_{24}N_2O_7)_2,H_2PtCl_6$, crystallises from hot dilute alcohol in needles, and melts at 203—205°. The *methiodide*, $C_{22}H_{24}N_2O_7,MeI$, crystallises from water in colourless prisms, and melts at 190°. F. S. K.

Cytisine and Ulexine. By A. Partheil (*Arch. Pharm.*, **230**, 448—498).—The author has already stated (Abstr., 1891, 231 and 750) that cytisine from laburnum and other varieties of *Cytisus* is identical with Gerrard's ulexine from *Ulex europæus*, and that it has the formula $C_{11}H_{14}N_2O$. For the preparation of the alkaloïd from either source, the pulverised seeds are extracted in a percolator with 60 per cent. alcohol acidified with acetic acid; chloroform is to be recom-

mended for extracting the free base, but its application, in the manner described by Buchka and Magalhaës (Abstr., 1891, 587), is not desirable, as an emulsion is formed. Gerrard and Symon state that a second base is present along with ulexine in the seeds of *Ulex europæus*, but the author failed to recognise it; he has, however, separated choline from the seeds of the *Cytisus* species.

Small quantities of cytisine base may be freed from the accompanying colouring matters by crystallisation from boiling light petroleum; the pure base crystallises from absolute alcohol in large, colourless, anhydrous prisms which are not deliquescent, melts at 152—153°, and is readily soluble in water, alcohol, and chloroform, less so in benzene and amyl alcohol, almost insoluble in cold light petroleum, and insoluble in pure ether. Its specific rotatory power in aqueous solution is $[\alpha]_{D17°} = -119{\cdot}57$, and analysis confirmed the formula given above. For the detection of the alkaloïd, Magalhaës' reaction serves; this consists in adding thymol to a solution of cytisine in concentrated sulphuric acid and heating, when a yellow coloration, finally passing into an intense red, is produced.

The author next describes a number of derivatives of cytisine, most of which are already known, and compares them with the corresponding derivatives of ulexine, thereby proving the identity of the two alkaloïds. Among these are the nitrate, $C_{11}H_{14}N_2O,HNO_3 + H_2O$, which has a specific rotatory power in aqueous solution $[\alpha]_{D17°} = -82{\cdot}4$, the two platinochlorides, $(C_{11}H_{14}N_2O)_2,H_2PtCl_6$ and $C_{11}H_{14}N_2O,H_2PtCl_6 + 2\frac{1}{2}H_2O$, the aurochloride melting at 212—213°, the acetyl derivative melting at 208°, and the methiodide which melts at 270° (compare Buchka and Magalhaës, Abstr., 1891, 587 and 750). Methylcytisine melts at 134°; the platinochloride crystallises with $2\frac{1}{2}$ mols. H_2O, and the aurochloride melts at 196° (*loc. cit.*). Ethylcytisine is a yellow liquid, and yields a platinochloride which crystallises with 1 mol. H_2O. Magalhaës' dimethylcytisine forms a platinochloride crystallising with $2\frac{1}{2}$ mols. H_2O, and gives rise to dimethylcytisine methiodide when heated on the water-bath with methyl iodide; the methiodide decomposes on boiling with concentrated aqueous potassium hydroxide with the evolution of trimethylamine, whilst chloroform extracts from the cold solution a base giving an amorphous, yellow platinochloride, $(C_{10}H_{13}NO_2)_2,H_2PtCl_6$. On distilling cytisine with soda lime, a base, $C_9H_{13}N$, probably a pyridine derivative, is obtained; this is, perhaps, related to the base $C_{10}H_{13}NO_2$, just mentioned. The alkaloïd gives no evidence of the presence of the group CO, in that it does not react with phenylhydrazine.

The precise constitution of cytisine is still obscure, but its behaviour towards methyl iodide, acetic anhydride, and nitrous acid (*loc. cit.*) shows that one of its nitrogen atoms is in secondary combination; the second nitrogen atom is either in tertiary or quaternary combination. That the oxygen atom exists neither in the form of methoxyl nor hydroxyl is proved by the fact that methylcytisine does not yield an acetyl derivative. The research is being continued.

A. R. L.

Organic Chemistry.

Action of Stannic Chloride on Halogen Derivatives of Methane. By G. GUSTAVSON (*J. Russ. Chem. Soc.*, **23**, 253—258).—When stannic chloride (1 mol.) is heated with carbon tetrabromide (1 mol.) at the temperature of boiling aniline (184°) for an hour, 26·16 per cent. of the chlorine in the chloride is replaced by bromine. Under similar conditions, only 0·7 per cent. of the halogens are interchanged when stannic chloride and bromoform are heated together in such proportions that the halogens in the two substances are equivalent.

The action in the case of methylene bromide is also slight, 1·05 per cent. of the halogens changing places.

When the mixtures of the chloride with bromoform and with methylene bromide are heated for 150 hours at 130—135°, the interchange takes place to the extent of 1·92 per cent. and 2·89 per cent. respectively. Titanium tetrachloride acts like stannic chloride; with bromoform, 3·54 per cent. of the chlorine is replaced after heating for 150 hours at 135°.

The following numbers were obtained with the iodine substitution products of methane after standing in the dark with stannic chloride for seven years:—Iodoform, no action; methylene iodide, 1·2 per cent.; methyl iodide, 34 per cent. J. W.

Preparation of Pure Chloroform from Salicylide Chloroform. By R. ANSCHÜTZ (*Ber.*, **25**, 3512—3513).—The author proposes to employ the compounds formed by salicylide and orthohomosalicylide with chloroform (this vol., i, 165) for the preparation of the latter substance in the pure state. These compounds, which contain about one-third of their weight of chloroform, are formed by simply boiling salicylide or orthohomosalicylide with chloroform for a few minutes; they can be preserved for any length of time in closed vessels without undergoing change, and readily give off chloroform on warming. The chloroform thus obtained remains unaltered on keeping, whereas the ordinary chloroform always becomes contaminated with carbonyl chloride. H. G. C.

Preparation of Silver Acetylide from Acetylenedicarboxylic acid. By W. LOSSEN (*Annalen*, **272**, 139—141).—Silver acetylide can be very easily prepared by gradually adding the theoretical quantity of a hot 10 per cent. solution of silver nitrate to a hot solution of sodium acetylenedicarboxylate; each addition of the silver solution produces a vigorous effervescence, due to the escape of carbonic anhydride, and the theoretical quantity of silver acetylide is obtained as a dirty yellow precipitate. F. S. K.

Action of Hydrogen Chloride and Hydrogen Bromide on Liquid α-Dichlorethyl Cyanide. By J. TROEGER (*J. pr. Chem.* [2], **46**, 353—380; compare Abstr., 1887, 1024).—When dry hydrogen

chloride is passed into liquid α-dichlorethyl cyanide, the sides of the flask become covered with crystals; the ultimate analysis of this substance, and determinations of its molecular weight by the cryoscopic method, indicate that it is *dimolecular α-dichlorethyl cyanide*, $(CMeCl_2CN)_2$. The new compound forms colourless, lustrous, monosymmetric crystals (measurements given), and begins to decompose at 130° without previous melting; it dissolves easily in cold methyl alcohol and molten phenol, but is insoluble in other organic solvents. When heated with sulphuric acid (1 : 1), it yields dichloropropionic acid (compare Otto and Voigt, Abstr., 1887, 1024). When shaken with water at the ordinary temperature, it partially dissolves, and crystals almost immediately begin to separate from the solution, which acquires a strongly acid reaction; the crystals dissolve readily in organic solvents, but cannot be purified by recrystallisation, inasmuch as no sharper melting point than 75—79° can be thus obtained; by dissolution in sodium hydroxide and reprecipitation with hydrochloric acid, the crystals can be obtained of constant melting point, 82—83°. The ultimate analysis and molecular weight determination of this substance show that it is *α-dichloropropionyl-hydroxyethyl cyanide*, $CMeCl_2{\cdot}CO{\cdot}CMe(CN){\cdot}OH$; when it, or the dimolecular α-dichlorethyl cyanide, is heated with water, it is converted into α-dichloropropionamide (m. p. 114°, generally given as 116°).

Another new *compound*, $C_6H_5Cl_3N_2$, is obtained in lustrous, prismatic needles, which melt at 48°, and dissolve in most solvents, when dimolecular α-dichlorethyl cyanide is treated with alcoholic ammonia; it has not been further investigated. When the cyanide is suspended in light petroleum, and subjected to the action of dry ammonia, a yellowish-brown oil is obtained; the analyses of this gave ill-defined results, but from the fact that two molecular proportions of ammonium chloride are eliminated, the author concludes that its formula is $C_6H_4Cl_2N_2$, and is confirmed in this opinion by the fact that it is converted into a chloracrylic acid by the action of sulphuric acid; the oil is volatile with steam, and the distillate partially solidifies, the solid portion having a poppy-like odour.

The action of hydrogen bromide on liquid α-dichlorethyl cyanide produces a *compound*, $C_6H_6Cl_2Br_2N_2$, which is very similar in all respects to dimolecular dichlorethyl cyanide; it has no definite melting point. It dissolves in methyl alcohol and molten phenol; from its solution in the former, it cannot be precipitated by ether, in which respect it differs from the chloro-derivative. The product of its decomposition with water melts at about 73°, and has a chlorine content corresponding with α-dichloropropionylhydroxyethyl cyanide (see above). During the action of the hydrogen bromide, a by-product, $C_3H_7Cl_2BrN_2$ (?), which crystallises in large, slender, white, tabular prisms, and melts at 147—148°, is formed; by the action of aqueous ammonia, it yields α-dichloropropionamide. A. G. B.

Reactions of Ferric Salts with Thiocyanates. By H. M. Vernon (*Chem. News*, **66**, 177—179, 191—193, 202—203, 214—215). —In these investigations, colorimetric observations were adopted for

comparison, and were made in vertical, flat-bottomed tubes, by comparing the solution to be tested with an adjustable column, either of a 0·1 per cent. solution of picrocarmine, or, in some cases, of a dilute solution of ferric thiocyanate, prepared from lithium thiocyanate and excess of ferric chloride. Solutions were examined containing 1, 2, 4, 7, 11, 18, 30, and 100 equivalents of ferric chloride to 1 part of potassium thiocyanate, and diluted to various degrees, ranging from 2- to 120-fold. In equivalent quantities, these two reagents react almost completely at infinite concentration, to form ferric thiocyanate; but solutions less dilute than those mentioned above were too deep in colour, whilst solutions containing one or two equivalents of ferric chloride, when diluted above 40 times, were too weak in tint for colorimetric examination. The decrease in ferric thiocyanate coloration, resulting from the dilution of the solutions from 8- to 120-fold, in the strongest solution, was 27 per cent., in the 30 : 1 solution over 60 per cent., in the 18 : 1 solution 73 per cent., whilst diluting from 2- to 32-fold in the case of the 1 : 1 solution resulted in a reduction of the coloration, amounting to 94 per cent.; the stability of the ferric thiocyanate, therefore, appears to vary regularly with the amount of ferric chloride present; moreover, the amount of ferric thiocyanate formed in these solutions varies with the dilution in accordance with the law of mass. The action of ferric chloride is twofold; in most cases it forms a solution in which the ferric thiocyanate is more stable than in pure water, but in very strong solutions, it exerts a decolorising and presumably a destructive action on the deep-coloured thiocyanate.

The examination of a similar set of solutions, in which the proportion of ferric chloride was kept constant, and that of the potassium thiocyanate varied, indicated that, although the ferric thiocyanate was more stable in a solution of potassium thiocyanate than in water, yet the decrease in colour on dilution did not, in this case, follow the law of mass, probably owing to the presence of impurities.

Numerous other experiments with various ferric salts and thiocyanates led to the following conclusions:—That the colour reactions of ferric chloride, nitrate, sulphate, tartrate, citrate, and acetate with potassium, ammonium, sodium, lithium, calcium, and barium thiocyanates, indicate that the formation of ferric thiocyanate in these cases is dependent on two factors, one being the nature of the acid of the ferric salt, the other the nature of the base of the thiocyanate; the former exerting an action somewhat in accord with the relative affinities of the acids, whilst the latter shows no such relationship. In all these cases, except with the acetate, the colour of the ferric salt caused no inconvenience.

Heating the solutions increases the activity of the various reactions, and when those that favour the formation of ferric thiocyanate predominate, an increase of colour is observed, and *vice versâ*. Therefore, by heating at 20°, 30°, 40°, 50°, and 60°, or when decomposition ensued at some intermediate temperature, an increase of colour is observed with thiocyanates and ferric salts of monobasic acids, and a decrease with ferric salts of polybasic acids. D. A. L.

Acid of Zinc Ethide on Acid Chlorides. By A. GRIGOROVITCH and D. PAVLOFF (*J. Russ. Chem. Soc.*, **23**, 159—178).—Isobutyric chloride (1 mol.) and zinc ethide (2 mols.) were brought together in a flask at a low temperature and allowed to remain for three days at 0°, the temperature being subsequently raised to about 18°. After a week, ethylene began to be evolved from the mixture, the evolution continuing for a long time; on the expiry of 30—35 days, the contents of the flask began to thicken, and after 65 days, had become gelatinous. Three months later, the products of the reaction were treated with ice and water, when an oily layer separated, having a caustic taste and the odour of camphor; this was distilled with steam, separated by means of potash, carefully dried, and fractionated. On continued fractionation, it separated into four portions boiling at 77—79°, 114—115·5°, 126—127°, and 158—161° respectively. The liquid boiling at 77—79° was proved to be ethyl alcohol, and that boiling at 114—115° was a ketone of the composition $C_6H_{12}O$; as the latter yielded acetone, isobutyric acid, and formic acid on oxidation with chromic mixture, it was ethyl isopropyl ketone.

Ethylisopropylcarbinol.—This was the chief constituent of the fraction which boiled at 126—127°. It is a colourless liquid with a pleasant ethereal odour resembling that of peppermint and a somewhat caustic taste, it boils at 127—127·5° under a pressure of 721 mm., and becomes viscid in a mixture of ice and salt. Its sp. gr. at 0°/0° is 0·8383, and at 20°/20° 0·8243, the mean coefficient of expansion for this range of temperature being 0·000904. The vapour density corresponds with the formula $C_6H_{14}O$.

The *acetate*, $CHPr^{\alpha}Et{\cdot}OAc$, prepared by boiling the alcohol for 15 hours with acetic anhydride, is a liquid of fruity odour, boiling at 148—148·5° (at 747 mm.) and remaining mobile at −21°. Its sp. gr. is 0·8856 at 0°/0° and 0·8688 at 20°/20°.

The corresponding chloro-derivative, *ethylisopropylchloromethane*, prepared by the action of phosphorus pentachloride on the alcohol, is a colourless liquid boiling with partial decomposition at 115—116·5°, and not solidifying at −21°. The *iodide*, formed by passing hydrogen iodide into the alcohol, is a reddish liquid, readily giving off hydrogen iodide, and reacting with water with development of heat. It boils with decomposition at 142—147°, and remains liquid at −21°.

The etherification constant of the alcohol is 0·00328 for molecular proportions of carbinol and acetic anhydride in 15 vols. of benzene at 100°. The carbinol was oxidised with a 10 per cent. solution of sulphuric acid and the quantity of potassium dichromate necessary to yield 1 atom of oxygen per molecule of alcohol; the chief product of oxidation was ethyl isopropyl ketone. With a larger proportion of the oxidising agent, the products were the same as those obtained on the oxidation of ethyl isopropyl ketone.

Diethylisopropylcarbinol.—The fraction boiling at 158—161° was left for 24 hours over baryta, and then boiled with it for four hours in order to remove the ethylisopropylcarbinol. The residual liquid, diethylisopropylcarbinol, boils at 159·5—161° under a pressure of 750 mm., and becomes viscid at −21°. It has an odour resembling that of camphor, and a caustic taste. Its sp. gr. at 0°/0°

is 0·8463 and at 20°/20°, 0·8295. The corresponding chloro-derivative is a colourless liquid, which becomes brown if left over calcium chloride, and is decomposed by water, especially on heating. It cannot be distilled, as it boils with decomposition at 150—155° with rapid evolution of hydrogen chloride. The iodo-compound is a brown liquid heavier than water, by which it is easily decomposed. In the air, it fumes and smells of garlic, the vapours producing a headache. The constant of etherification of the alcohol, under the same conditions as those given above for ethylisopropylcarbinol, is 0·00056. On oxidation with 3 atoms of oxygen (from potassium dichromate and 10 per cent. sulphuric acid solution) per molecule, the alcohol yielded carbonic anhydride, acetone, and propionic, acetic, and formic acids. Amongst the products of oxidation was an unsaturated hydrocarbon identical with that obtained from the chloro-derivative by the action of alcoholic potash. This hydrocarbon proved to be *asymmetrical dimethyldiethylethylene*, $CMe_2{:}CEt_2$. It boils at 114·5—116·5° under 741 mm. pressure, and readily combines with bromine. The authors attempted to convert this unsaturated hydrocarbon into dimethylsecondaryamylcarbinol by heating it with fuming hydriodic acid and treating with silver oxide. The bulk of the product, however, was the original hydrocarbon, only a small quantity of a liquid boiling at 158—161° being obtained; this had the odour of a tertiary alcohol.

By means of Meyer and Locher's reaction, the authors were able to prove that a secondary alcohol is formed in the reaction between zinc ethide and acetic chloride, although only in very small quantity.

J. W.

Psyllostearyl Alcohol. By E. E. Sundwik (*Zeit. physiol. Chem.*, **17**, 425—430).—In Finland, in summer, the trunks of the *Alnus incana* were observed to be covered with a white powder, which was found to be the result of the presence on them of the louse, *Pysllа alni*, being a secretion from glands on its back.

A large quantity of this was collected, and a crystalline substance separated from it. It is soluble in hot chloroform, acetic anhydride, sparingly soluble in hot absolute alcohol and in ether, and not at all in cold or hot spirit. It gives no reaction of cholesterol. It melts at 95—96°, and does not give an acetyl derivative. Elementary analysis of it, and its bromine derivative, showed its simplest formula to be $C_{28}H_{56}{\cdot}OH$. It probably is a new member of the fatty alcohols, and the name *Psyllostearyl alcohol* is given to it. W. D. H.

Synthesis of Sugars. By W. E. Stone (*Chem. News*, **66**, 165—166, 179—180, 194).—A valuable *résumé* of recent work on this subject.

Birotation and Hydrazone Formation of some Sugars. By H. Jacobi (*Annalen*, **272**, 170—182).—A study of the change in rotatory power of solutions of sugars which have just been mixed with solutions of phenylhydrazine has shown that the hydrazone formation invariably takes place more quickly in the case of a freshly

prepared sugar solution than in that of a solution which has been kept for some time; this fact affords support to the theory that birotation is due to the combination of the solvent with the optically active substance.

The modification of glucosephenylhydrazone melting at 113—115° has, in freshly prepared aqueous solution, a specific rotatory power $[\alpha]_{D20°} = -15{\cdot}3°$; after 12—15 hours, the specific rotatory power has become constant and is then $[\alpha]_D = -46{\cdot}8°$.

Galactosephenylhydrazone has a specific rotatory power $[\alpha]_{D20°} = -21{\cdot}6°$, that of rhamnosephenylhydrazone being $[\alpha]_{D20°} = -54{\cdot}2°$; neither compound shows birotation.

A freshly prepared aqueous solution of crystalline rhamnose, $C_6H_{12}O_5 + H_2O$, is lævorotatory, but after about an hour's time the specific rotatory power has become constant at $[\alpha]_{D20°} = +8{\cdot}3°$; rhamnose which has been melted or dried for a long time does not show birotation in aqueous solution. In alcoholic solution, crystalline rhamnose shows birotation, the specific rotatory power being $[\alpha]_{D20°} = -11{\cdot}4°$ 15 minutes after solution, and becoming constant at $[\alpha]_{D20°} = -9°$ after 16 hours. Anhydrous rhamnose also shows birotation in alcoholic solution, the initial and final values of the specific rotatory power being $[\alpha]_{D20} = +3{\cdot}4°$ and $-9°$ respectively.

When a freshly prepared aqueous solution of dextrose is mixed with a solution of an equal weight of phenylhydrazine in dilute acetic acid, and the mixture examined optically, the rotation is observed to change rapidly, becoming constant after about two hours; from the end value, the specific rotatory power of the hydrazone is calculated to be $[\alpha]_{D20°} = -47°$, so that the interaction of the sugar and the hydrazine takes place quantitatively.

The rotation of a mixture of an aqueous solution of dextrose, which has been kept for 24 hours, with a solution of phenylhydrazine in dilute acetic acid also changes on keeping, but much more slowly than in the preceding case, owing to the fact that hydrazone formation takes place much more slowly; after about $5\frac{1}{2}$ hours, a constant end value, about the same as in the preceding case, is attained.

Similar results are obtained in studying the rotation of solutions of galactose and phenylhydrazine; when a freshly prepared solution of the sugar is used, the specific rotatory power becomes constant after about $2\frac{1}{2}$ hours, being then approximately $[\alpha]_{D17{\cdot}5°} = -19{\cdot}2°$; as the specific rotatory power of galactosephenylhydrazone is $[\alpha]_D = -21{\cdot}6°$, it is clear that the action does not take place quantitatively.

When a galactose solution, which has been kept for 24 hours before adding the phenylhydrazine solution, is used, about $4\frac{3}{4}$ hours elapse before the specific rotatory power becomes constant at $[\alpha]_{D17{\cdot}5°} = -18{\cdot}4°$.

Observations with mixed solutions of rhamnose and phenylhydrazine show that in this case also the freshly dissolved sugar combined more rapidly with the hydrazine than the sugar which had been dissolved for 24 hours; in both cases, however, a constant rotation is attained very quickly, the end value being that of rhamnosephenylhydrazone. F. S. K.

Non-crystallisable Products of the Action of Diastase on Starch. By A. SCHIFFER (*Chem. Centr.*, 1892, ii, 825—826; from *Neu Zeit. Ruben-Zuck.-Ind.*, **29**, 167—170).—The author has endeavoured to obtain Brown and Morris's maltodextrin by the action of diastase on potato starch, but without success; neither has he been able to prepare the so-called amyloïns. He finds that isomaltose is formed, not maltose, and considers it probable that Brown and Morris's maltodextrin was a mixture of 67 per cent. of dextrin with 33 per cent. of isomaltose, whilst Herzfeld's maltodextrin consisted of 74 per cent. of isomaltose and 26 per cent. of dextrin.

The experiments on the dextrins did not lead to very definite conclusions. The achroödextrin obtained showed a rotatory power of $[\alpha]_D = 189{\cdot}99°$, and, in 3 per cent. solution, a reducing power of 12·523 per cent. on the dry substance calculated as maltose; it did not colour iodine. A non-reducing dextrin could not be obtained. The erythrodextrin obtained had a rotatory power of $[\alpha]_D = 191{\cdot}27°$, and a reducing power, in 4·7 per cent. solution, equivalent to 5·68 per cent. on the dry substance calculated as maltose; it gave a red coloration with iodine. The dextrins are not fermentable, and it would seem that there are only a small number, probably not more than two; at present, there is only evidence for the existence of one dextrin not giving a coloration with iodine.

Isomaltose invariably occurs amongst the transformation products of starch. A. J. G.

Action of Dilute Acids and Alkalis on Cellulose. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, **17**, 391—400).—Cellulose, prepared from various sources, was subjected to the action of acids and alkalis of different strengths. The loss so produced is stated in the form of tables. The results obtained confirm the statements of earlier observers, that cellulose is but very slightly attacked by very dilute, hot, mineral acids. With alkalis (5—10 per cent.), the cellulose is considerably dissolved, but this again is confirmatory of the earlier work on the subject with impure material. W. D. H.

Vegetable Amyloïd. By E. WINTERSTEIN (*Zeit. physiol. Chem.*, **17**, 353—380).—Amyloïd is the name given by botanists to the constituent of cell walls, which, like starch, is coloured blue by iodine, and so differs from cellulose.

In the cotyledons, from which it was prepared in the present research, it serves as a reserve material, according to some, as a reserve cellulose. The seeds worked with were those of *Tropæolum majus*, *Pæonia officinalis*, and *Impatiens balsamina*. After its separation (the method used is fully described), it is precipitable from its aqueous solution by alcohol. The precipitate is very voluminous. It is amorphous after drying over sulphuric acid. It swells in cold, and forms an opalescent solution in hot, water. Even after the prolonged action of diastase, or boiling with water in a digester, it does not reduce Fehling's solution. The solution, after boiling in a digester, becomes clearer. $[\alpha]_D = +92—94°$.

Elementary analysis gave C 43·17, H 6·08, per cent. By oxidation with nitric acid, it yields mucic acid.

In opposition to earlier investigations, it was found that, after inversion with sulphuric acid, dextrose was not formed, or only in minimal quantities; the sugars formed are two in number: one is galactose, the other a pentose, xylose.

It is difficult to say whether amyloïd is a single chemical substance; it belongs to Tollens' class of polysaccharides, and especially to the saccharo-colloïds.

After the extraction of amyloïd from the seeds, the carbohydrate residue consists of Schulze's hemicelluloses. These substances, after inversion, were also found to yield galactose and xylose.

W. D. H.

Parent Substance of Wood Gum. By E. Winterstein (*Zeit. physiol. Chem.*, **17**, 381—390).—Wood gum, or xylan, is the material obtained from wood by extracting it with cold 5 per cent. sodium hydroxide and then precipitating with alcohol and hydrochloric acid. On inversion it yields xylose.

By treating powdered beech wood with Schulze's reagent, the residue still contains, or yields, xylan. Xylan is present in at least two modifications, one of which is destroyed by boiling with dilute acids, or by Schulze's reagent, and the other resists these. The latter parent substance of xylan appears to be cellulose. The other is probably a modification of cellulose. W. D. H.

Molecular Compounds of Amines. By W. Rudnew (*J. pr. Chem.* [2], **46**, 305—316).—The compounds obtained by mixing alkyl iodides with amines at the ordinary temperature are not salts of imide bases, as previously supposed by the author (*J. Russ. Chem. Soc.*, **11**, 174), but are molecular compounds of the amine and its hydriodide. The reactions studied were those between (1) tertiary butyl iodide and tertiary butylamine, which react to form the compound $C_4H_9{\cdot}NH_3I,C_4H_9{\cdot}NH_2$; (2) tertiary amyl iodide and tertiary butylamine, which react to form the same compound as in (1); (3) tertiary butyl iodide and tertiary amylamine, which form the compound $C_5H_{11}{\cdot}NH_3I,C_5H_{11}{\cdot}NH_2$, accompanied by a little of the compound $C_5H_{11}{\cdot}NH_2(C_4H_9)I$; (4) isobutyl iodide and isobutylamine, which also form $C_4H_9{\cdot}NH_3I,C_4H_9{\cdot}NH_2$, but a considerable proportion of the secondary amine hydriodide, $NH_2(C_4H_9)_2I$, is produced at the same time. A. G. B.

Derivatives of Urethane. By A. Andreocci (*Real. Accad. Linc.*, 1892, i, 257—264).—The author prepares urethane by boiling carbamide nitrate with absolute alcohol and sodium nitrite under a pressure of 1·5 atmos. 70 per cent. of the theoretical yield may be obtained.

Acetylurethane is best prepared by heating urethane and acetic chloride in molecular proportion in a reflux apparatus.

Methylacetylurethane, NMeAc·COOEt, is obtained by heating an ethereal solution of acetylurethane with sodium and methyl iodide, or by heating methylurethane and acetic chloride in closed tubes at 100—105°. It is a liquid which boils at 125—127° under 63 mm. pressure, and is very soluble in alcohol or ether. Atmospheric moisture slowly hydrolyses it, with formation of acetic acid and methylurethane.

Chloracetylurethane, $NH(CO\cdot CH_2Cl)\cdot COOEt$, is prepared by heating chloracetic chloride with urethane, or by the action of sulphuryl chloride on acetylurethane. It crystallises in prisms or rhomboidal laminæ melting at 127—128°, and sublimes at 100°; it is soluble in ether, alcohol, benzene, chloroform, or boiling water, and very sparingly so in cold water. It gives *sodio-* and *potassio*-derivatives, which are readily decomposed by water, and with sodium ethoxide yields ethylurethane.

Dichloracetylurethane, $NH(CO\cdot CHCl_2)\cdot COOEt$, is prepared by heating dichloracetic chloride with urethane, or by heating sulphuryl chloride with chloracetylurethane or acetylurethane. It separates from hot water in rhomboidal plates, melts at 93°, and is soluble in alcohol or ether, sparingly so in cold water. It gives a *sodio*-derivative with metallic sodium.

Trichloracetylurethane, $NH(CO\cdot CCl_3)\cdot COOEt$, is an oily liquid, best prepared by heating urethane with trichloracetic chloride. Heat converts it into a solid substance still under examination.

Acetylxanthamide, $NHAc\cdot CSOEt$, is obtained by heating xanthamide with acetic anhydride. It forms colourless scales, of pearly lustre, melts at 104°, and is soluble in alcohol, ether, ethyl acetate, or boiling water. W. J. P.

Condensation of β-Diketones with Carbamide and Thiocarbamide. By P. Evans (*J. pr. Chem.* [2], **46**, 352).—When acetylacetone (1 mol.) and carbamide (2 mols.) are mixed in alcoholic solution, and 10 drops of hydrochloric acid (sp. gr. 1·19) added, crystals of the condensation product, $CH_2(CMe{:}N\cdot CO\cdot NH_2)_2,HCl$, separate. When four times as much hydrochloric acid is used, the compound $CH_2<\begin{matrix}CMe{:}N\\CMe{:}N\end{matrix}>CO,HCl$ is formed. When sulphuric acid is substituted for hydrochloric acid, the corresponding sulphates are obtained.

Analogous compounds are prepared from acetylacetone and thiocarbamide.

Benzoylacetone and carbamide condense with difficulty; the direct product is $CPh\cdot O\cdot CH_2\cdot CMe{:}N\cdot CO\cdot NH_2$, which is split up by alkalis into $CH_2<\begin{matrix}CMe{:}N\\CPh{:}N\end{matrix}>CO$. These matters are being further investigated. A. G. B.

Derivatives of Ketopentamethylene and Ketohexamethylene. By F. W. Semmler (*Ber.*, **25**, 3513—3520).—In a recent paper (this vol. i, 107), the author has shown that when tanacetogendicarboxylic acid is heated with soda-lime it yields an oil having the composition $C_9H_{12}O$, and closely resembling camphorone. From its physical properties it appears to contain a ring of carbon atoms and also an ethylene linking, the most probable formula being $\begin{matrix}CH_2\cdot CH_2\\|\\CH_2\cdot CO\end{matrix}>CMe_2$, according to which it is *isopropeneketopentamethylene*. On oxidation with dilute potassium permanganate solution, it yields a lactone, having the composition $C_7H_{12}O_2$, which boils at 145°

under 11 mm. pressure, and melts at about the ordinary temperature. The author regards it as *δ-hydroxy-γ-isoheptylic lactone*, and supposes that the carbonyl group is eliminated as carbonic anhydride, and a hydroxyl group added to each of the carbon atoms combined by ethylene linkage, the acid $CMe_2(OH)\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COOH$ then losing water, and forming the lactone $\begin{matrix}CH_2\cdot CH_2\\ |\\ CO-O\end{matrix}>CH\cdot CMe_2\cdot OH$.

To obtain further evidence on the matter, the author has also investigated the pulegone obtained by Beckmann and Pleissner (Abstr., 1891, 936), which is probably a derivative of ketohexamethylene. In addition to the possible formulæ given by those investigators, the author gives a fourth, namely,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CO\end{matrix}>C:CMe_2;$$

the presence of the isopropene group, $:CMe_2$, being rendered probable by the fact that it yields acetone on oxidation. If this formula is correct, the other product of oxidation should be β-methyladipic acid, $COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot COOH$, and it was found on investigation that this acid is formed in almost quantitative proportions. On the addition of benzene to its solution in chloroform, it separates in colourless crystals melting at 84·5°, and boiling at 210—212° under 14·5 mm. pressure, and, like pulegone, rotates the plane of polarisation to the right. On further oxidation, the tertiary hydrogen atom in the CHMe group is oxidised to hydroxyl, the hydroxy-acid thus formed at once losing water, and forming *γ-valerolactone-γ-acetic acid*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CO-O\end{matrix}>CMe\cdot CH_2\cdot COOH$. β-Methyladipic acid is readily converted into the *diethyl* salt, which has a fruity odour, and boils at 126·5° under 10 mm. pressure.

When β-methyladipic acid is distilled with soda-lime, it yields a liquid which smells like camphorone, and boils at 141—143°; it is a ketone and a saturated compound, and must, therefore, from its method of formation, be *β-methylketopentamethylene*, $\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2-CH_2\end{matrix}>CO$. With hydroxylamine, it yields a mixture of two isomeric *oximes*, one of which melts at 81·5°, whilst the other has not yet been obtained pure. On reduction with sodium in alcoholic solution, the oximes are converted into *β-methylpentamethylenylamine*,

$$\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2-CH_2\end{matrix}>CH\cdot NH_2,$$

which is a liquid smelling like the fatty amines, and boiling at 42° under 12 mm. pressure. With nitrous acid, it yields the corresponding *β-methylpentamethylenol*, $\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2-CH_2\end{matrix}>CH\cdot OH$, boiling at 48—50° under 15 mm. pressure.

In conclusion, the author gives a table of constitutional formulæ, showing the relations between the compounds described in this and other papers and menthone, pulegone, camphoric acid, camphorone, &c. H. G. C.

Products of the Dry Distillation of Birch Bark. By V. KURILOFF (*J. Russ. Chem. Soc.*, **23**, 98—101).—Birch bark, on dry distillation, gives, besides tar, a considerable quantity of an acid aqueous solution. The author has investigated this solution for acids and for bases. He first of all distilled it, and neutralised the distillate with sodium carbonate, evaporated the salt solution thus obtained to dryness, heated the residue slightly in order to drive off phenols, dissolved it in water, and filtered to remove carbonaceous matter. The filtrate was acidified with phosphoric acid, and fractionally distilled. The distillates were further subdivided by fractional neutralisation and distillation, and the acids converted into the silver salts, which were then analysed. Scarcely any difference was observed between the fractions, the amount of silver contained in the salts being in all cases only slightly less than that required by silver acetate. The aqueous solution contains 1·25 per cent. of acetic acid.

The only volatile base found was ammonia, which is present in the solution to the amount of 0·73 per cent. J. W.

Preparation of Chloracetic acid. By A. RUSANOFF (*J. Russ. Chem. Soc.*, **23**, 222—223).—The chlorination of acetic acid may be readily effected by mixing the glacial acid employed with from $\frac{1}{12}$th to $\frac{1}{15}$th of its weight of red phosphorus. A rapid current of chlorine is passed into the mixture at 100°, the absorption being very complete. On cooling, the liquid solidifies to a white, crystalline mass, which is almost pure monochloracetic acid. With the above proportion of phosphorus, the quantity of chloro-acid obtained is about equal to the quantity of acetic acid taken. J. W.

Compounds of Copper Acetate with Ammonia and with Pyridine. By F. FOERSTER (*Ber.*, **25**, 3416—3422).—*Copper acetate ammonia*, $Cu(C_2H_3O_2)_2,2NH_3$, is prepared by adding an excess of alcoholic ammonia to an alcoholic solution of copper acetate (a certain quantity of copper oxide is formed when aqueous solutions are employed); after distilling off the excess of alcohol, the salt separates, and when recrystallised from alcohol, it is obtained in anhydrous, short, violet prisms or octahedra. It may be dried over sulphuric acid in a vacuum. Schiff (*Annalen*, **123**, 43) has described a hydrate of this compound, crystallising with 2 mols. H_2O, which he obtained by allowing an aqueous ammoniacal solution of copper acetate to evaporate at the ordinary temperature. The author finds that the anhydrous compound separates from concentrated aqueous solutions, whilst a hydrate, crystallising in blue needles with $2\frac{1}{2}$ mols. H_2O, and having crystallographic relations agreeing with those observed by Schiff for his compound, is obtained from dilute solutions. The copper acetate ammonia gradually loses ammonia in moist air, and deliquesces; it dissolves in water, forming a deep blue solution, which on dilution yields a bright blue jelly; the latter changes after a time into a fine powder, consisting of a basic copper acetate. It deliquesces rapidly in contact with aqueous ammonia, but undergoes no chemical change. When dry gaseous ammonia

is passed over anhydrous copper acetate, or better over the above described anhydrous copper acetate ammonia, it is absorbed with the evolution of heat. In the second case, the colour of the compound changes to blue, and a compound, probably $Cu(C_2H_3O_2)_2,4NH_3$, is produced; it, however, quickly dissociates in the air into ammonia and the compound $Cu(C_2H_3O_2)_2,2NH_3$; a compound containing less ammonia than the latter could not be obtained.

Copper acetate pyridine, $Cu(C_2H_3O_2)_2,C_5NH_5$, separates in lustrous, pure blue, six-sided tables, when pyridine is added to an aqueous or alcoholic solution of copper acetate, and the mixture evaporated. It remains unaltered over concentrated sulphuric acid in a vacuum, but undergoes slight decomposition when heated at 100°. It may be crystallised from hot water, and is only slightly decomposed when boiled with that solvent for a long time; it, however, suffers more decomposition when dissolved in boiling alcohol. When finely pulverised copper acetate is triturated with an excess of pyridine, a blue compound, $Cu(C_2H_3O_2)_2,4C_5NH_5$, is obtained; it gradually loses 3 mols. of pyridine on remaining in the air.

The blue liquid used for filling thermometer tubes often consists of an alcoholic solution of copper acetate ammonia, and when the instrument is constructed of bad glass, the free alkali causes a precipitation of basic copper acetate, or copper oxide. The means of preventing such precipitations will form the subject of a future communication.

Crystallised copper acetate (1 mol. H_2O) remains constant in weight when kept over concentrated sulphuric acid in a vacuum, as stated by Roux (*Annalen*, **60**, 316), but it is slowly dehydrated at 100°, more rapidly at 105°; the anhydrous salt is green.

A. R. L.

The Behaviour of α-Amidopropionic acid at High Temperatures. By E. Drechsel (*Ber.*, **25**, 3502—3504).—When a solution of α-amidopropionic acid in concentrated phosphoric acid is distilled, water at first comes over; the temperature then rises to 220—230°, decomposition sets in, and aldehyde, carbonic oxide, and ammonia are formed.

E. C. R.

Crotonic acids and their Derivatives. By A. Michael and O. Schultess (*J. pr. Chem.* [2], **46**, 236—266).—The details of the methods for preparing the crotonic acids given in this paper do not materially differ from those already published. Wislicenus and others (Abstr., 1887, 655; 1889, 236) have investigated the chlorination and bromination of crotonic and isocrotonic acids in carbon bisulphide and, in the case of isocrotonic acid, have obtained liquid acids which were regarded as αβ-isodichloro- and αβ-isodibromobutyric acids mainly on the ground that they were convertible into α-chloro- or α-bromo-crotonic acid, respectively, by the action of sodium hydroxide. Beside these, small quantities of the solid dichloro- and dibromo-butyric acids were obtained, and their formation was attributed to the presence of crotonic acid in the isocrotonic acid used. In their study of the same subject, the authors used

chloroform and carbon tetrachloride as solvents for chlorination experiments, and carbon bisulphide for bromination experiments; the products crystallised in all cases, and only in the chlorination experiments was any notable quantity of oily product obtained. They are, therefore, unable to confirm the existence of the liquid acids above referred to, and attribute their supposed formation to the presence of products of the action of the halogens on the carbon bisulphide or its impurities, which would be specially liable to occur in absence of bright light, and would hinder the crystallisation of the acids. Nor is Wislicenus correct in his statement as to the action of sodium hydroxide on the products in question (see above); a mixture of the normal and iso-acids is produced in each case, and in that of the chlorination product the mixture contains more of the iso-α-chlorocrotonic acid.

The above experiments were performed with an isocrotonic acid which, although containing less crotonic acid than that used by Wislicenus, was not perfectly pure, and the authors' attention was turned to the obtainment of a pure acid. When this acid was prepared, its chlorination and bromination gave results virtually identical with those outlined above. The purification was effected by means of the difference in solubility of the sodium salts in alcohol. At 11° 1 part of sodium crotonate dissolves in 380 parts of absolute alcohol, whilst 1 part of sodium isocrotonate dissolves in 16 parts.

In the aqueous mother liquor of the crotonic acid recovered from the crude isocrotonic acid by the new process, there was found a small quantity of tetrolic acid (m. p. 76°) which was at first mistaken for a new acid owing to the fact that it crystallises from light petroleum, together with crotonic acid (m. p. 72°), in prisms which melt at 83°; this is a notable instance in which a mixture of two substances melts at a higher temperature than does either constituent. The discovery that tetrolic acid is a secondary product of the action of sodium amalgam on β-chlorisocrotonic acid elucidates a difficulty noted by Geuther (*Zeit. Chem.*, 1871, 244) who, when reducing β-chlorocrotonic acid (m. p. 94°), obtained crystals which melted at 79° until they had been several times recrystallised, when the melting point dropped to 72°; a repetition of Geuther's experiments resulted in the isolation of tetrolic acid (compare Fittig and Clutterbuck, Abstr., 1892, 961). It was not found possible to avoid the formation of tetrolic acid during the reduction of β-chlorisocrotonic acid.

Pure isocrotonic acid boils at 74° under 15 mm. (bath at 85°) and at 78·5° under 20 mm. (bath at 90°); the *silver salt* is a white, curdy precipitate, which crystallises from hot water in lustrous needles. When the acid is heated for 36 hours in a sealed bulb at 100°, it undergoes no change; under the same conditions at 136°, 34 per cent. of it is converted into the solid crotonic acid, whilst at 162° and 182°, 66 per cent. and 67·5 per cent., respectively, are so converted (compare Alberti, *Ber.*, **9**, 1194); in the presence of a trace of iodine, the conversion takes place to a slight extent at 100°. Comparative experiments were made concerning the elimination of chlorine from β-chlorocrotonic acid (m. p. 94°) and β-chlorisocrotonic acid (m. p. 61°) by 10 times their weight of 30 per cent. sodium hydroxide solu-

tion, care being taken to avoid rise of temperature; it was found that, after 14 days, the β-chlorocrotonic acid had lost 95 per cent., and the β-chlorisocrotonic acid 88 per cent. of its chlorine. The influences of time and concentration were also studied, and the results are tabulated.

Experiments are detailed which prove that $\alpha\beta$-dichlorobutyric acid (m. p. 63°) yields, contrary to Wislicenus' statements (Abstr., 1887, 655; 1889, 236), a mixture of α-chlorocrotonic and α-chlorisocrotonic acids when treated with either warm or cold sodium hydroxide. When $\alpha\beta$-dibromobutyric acid is thus treated, only some 3·5 per cent. of α-bromocrotonic acid is produced, the rest being α-bromisocrotonic acid (m. p. 92°). Melikoff's experiment of heating α-chlorocrotonic acid with hydrochloric acid (compare Abstr., 1886, 1008) was repeated; the $\alpha\beta$-isodichlorobutyric acid thus obtained crystallises in prisms, melts at 78° (Melikoff gave 72—73°; Abstr., 1892, 296), and distils at 131·5° under 20 mm. (bath at 145°). The isolation of this second solid $\alpha\beta$-dichlorobutyric acid is evidence that Wislicenus' liquid acid has no existence.

$\alpha\beta$-Isodibromobutyric acid was prepared by heating α-bromocrotonic acid with hydrobromic acid at 100° in a sealed tube for 20 hours; it crystallises in small needles, melts at 58—59°, and is more soluble than the known acid (m. p. 87°). With alkalis, it yields a mixture of α-bromocrotonic acid and α-isobromocrotonic acids. $\alpha\beta$-Dibromobutyric acid (m. p. 87°) is partly converted into this acid (m. p. 58—59°) when heated with hydrobromic acid.

As is already known (Abstr., 1883, 969), β-chlorocrotonic acid is partially converted into β-isochlorocrotonic acid when heated; but α-isobromocrotonic acid is entirely converted into α-bromocrotonic acid when heated in boiling xylene. A. G. B.

Formation of Solid Crotonic acids by the Reduction of α-Isobromo- and α-Isochloro-crotonic acids. By A. Michael (*J. pr. Chem.* [2], **46**, 266—272).—The author quotes experiments which show that α-isobromocrotonic acid is converted almost entirely into solid crotonic acid when reduced by sodium amalgam, whether in acid or alkaline solution. α-Isochlorocrotonic acid also yields much more solid than liquid crotonic acid when similarly reduced. This repetition (compare Abstr., 1888, 1176) is rendered necessary by Wislicenus' criticisms (*Annalen*, **248**, 352). A. G. B.

Addition of Bromine and Chlorine to Solid Crotonic acid. By Mrs. H. A. Michael (*J. pr. Chem.* [2], **46**, 273—285; compare preceding abstracts).—The experiments detailed in this paper were undertaken as part of the controversy between Michael and Wislicenus, and have special reference to the remarks of the latter in *Annalen*, **248**, 281. The tabulated results show that the addition of chlorine and bromine to solid crotonic acid is accompanied by fewer secondary reactions when allowed to proceed rapidly in a well cooled solution exposed to direct sunlight. The $\alpha\beta$-dihalogen butyric acid produced, when the reaction was normal, was accompanied by some

10 per cent. of the iso-acid in the chlorination experiments, and by some 3 per cent. in the bromination experiments. A. G. B.

Brom-additive Products of Angelic and Tiglic acids. By J. WISLICENUS (*Annalen*, **272**, 1—99).—Fittig (Abstr., 1891, 39) attempted to show that the results obtained by the author and Pückert (Abstr., 1889, 587), in studying the action of bromine on angelic acid, were inaccurate; he claimed to have proved that tiglic acid dibromide, and not angelic acid dibromide, is produced by the action of bromine on angelic acid, and at the same time he made several statements reflecting very seriously on the author. The first portion of the paper is devoted to a refutation of these statements.

In preparing angelic and tiglic acids from various samples of Roman oil of chamomile by several different methods, it was found that, not only was the composition of the oil very variable, but that the yield of the two acids depended very much on the method of treatment; the total yield of crude, oily acid product, obtained by hydrolysing the oil with alcoholic potash, and weighed moist, was always between 49 and 51 per cent. of the oil, but the relative quantities of the several constituents were very variable. Many oils contained very little methacrylic acids, others a great deal. The fraction of the oily acid product which boiled above 175° always contained angelic acid as principal constituent; tiglic acid, if present, occurred in smaller quantities, and sometimes seemed to be absent altogether from the original oil. The yield of tiglic acid increased with the quantity of potash employed in hydrolysing, with the duration of the heating, and even more with the duration and frequency of the subsequent fractional distillation, the quantity of angelic acid becoming correspondingly smaller. When a good yield of angelic acid is desired, a preliminary partial separation of the two acids by means of their calcium salts is to be recommended, although this method is not so satisfactory as would appear from Pagenstecher's description; when tiglic acid is also required in quantity, Kopp's method of preparation is to be preferred.

From observations made with a large number of compounds, it has been found that, in order that the formation of additive products of unsaturated compounds may take place in the simplest manner, and without intramolecular change, the reaction must be carried out at the lowest possible temperature, and light excluded as far as possible; further, that the halogens and halogen acids, which are to be combined with the unsaturated compound, must always be present in large excess.

Under these conditions, and employing pure and dry substances and solvents, the pure dibromo-additive products of angelic and tiglic acids can be easily prepared.

The preparation of these compounds is then described in great detail. Briefly, the method was to slowly add, with frequent shaking, very small quantities of a solution of the acid in carbon bisulphide to a solution of not less than $1\frac{1}{2}$ mols. of bromine also dissolved in carbon bisulphide, in absence of moisture and in a very dim light, the temperature being kept below 10°; after the whole of the acid was

added, an operation which required 1½ to 2 hours, the mixture was kept over night, and the carbon bisulphide and excess of bromine then evaporated in a stream of dry air, one vessel being used for the whole process. Under these conditions, which will hereafter be referred to as normal, the yield of crude tiglic acid dibromide is only a few tenths per cent. below the theoretical, a trace of some substitution or decomposition product being also formed with evolution of hydrogen bromide; the yield of crude angelic acid dibromide, on the other hand, is rather more than the theoretical, owing to the difficulty of expelling all the carbon bisulphide.

The two acids show, even up to this point, a totally different behaviour. The solution of the tiglic acid dibromide begins to crystallise long before the whole of the carbon bisulphide is evaporated, and a snow-white dibromo-derivative, identical with the compound described by Pagenstecher (Abstr., 1879, 455), as was found by Pückert, is obtained. The solution of the angelic acid dibromide, on the other hand, yields, on evaporation, a brown oil, but, on continuing to pass a stream of dry air for a long time, crystallisation begins at the edges and gradually proceeds, accompanied by a continual decrease in weight; when, however, the oil is placed over soda-lime under reduced pressure, it soon froths up, gradually becomes thick, and finally solidifies to a hard, yellow mass, which still smells of bromine and carbon bisulphide.

The tiglic acid dibromide, after recrystallisation from light petroleum (b. p. 60°), melts at 87—88°, and does not liquefy on treatment with water.

The crude crystalline angelic acid dibromide is best freed from most of its carbon bisulphide by repeatedly treating it with petroleum pentane (b. p. 25—33°), and evaporating the latter in a rapid stream of air; it can then be recrystallised from warm petroleum pentane (b. p. 33—39°). When this purification is repeatedly carried out, in absence of moisture, and the crystals then freed from petroleum and carbon bisulphide in a desiccator under reduced pressure, a compound is obtained melting constantly at 86·5—87°, but the least trace of moisture lowers the melting point very considerably.

As the yield of pure substance is more than 90 per cent. of the crude product, further quantities of the pure compound being obtainable from the mother liquors, the author is absolutely convinced that a homogeneous substance, differing considerably in properties from tiglic acid dibromide, can be obtained from angelic acid in the manner described.

The two dibromides show a considerable difference in behaviour in passing from the liquid to the solid condition. The tiglic acid dibromide solidifies to an opaque, crystalline mass. The angelic acid dibromide forms an amorphous, resinous mass which becomes crystalline after some time; this amorphous dibromide is much more readily soluble in light petroleum than the crystalline variety, and on quickly evaporating its almost saturated solution, it is again deposited in an amorphous condition. When the solution of the amorphous substance is kept in a closed vessel, it begins to deposit crystals after some time, and, if the mother liquors are evaporated soon after the

first separation of crystals occurs, an amorphous, gum-like mass is obtained, in which crystals are embedded; if, on the other hand, the mother liquors are not evaporated until after long keeping, only the crystalline dibromide is deposited.

The most striking difference in properties between the two dibromides is in their behaviour with water. Whereas tiglic acid dibromide is sparingly soluble in, but is not otherwise changed by, water, and separates from its aqueous solution in crystals, angelic acid dibromide slowly liquefies when kept in an atmosphere saturated with aqueous vapour, and is immediately converted into a highly refractive oil in contact with water. This oil seems to be an unstable compound, probably of the composition $C_5H_{10}Br_2O_3$; it decomposes in moderately dry air or when treated with concentrated hydrochloric acid, yielding crystals of the dibromide, but, when kept at 0° in a closed vessel, it does not show the least signs of crystallising.

The solubility of the two dibromides in water, benzene, carbon bisulphide, and light petroleum is also very different, as was proved by careful determinations at various temperatures; the following table shows the solubility in 100 parts of the several liquids.—

	Water.	Petroleum pentane.	Benzene.	Carbon bisulphide.
Angelic acid dibromide	2·46 at 16° 2·63 at 20°	35·22 at 8° 138·9 at 20°	437·74 at 14·5° 542·52 at 21·5°	315·27 at 3° 472·29 at 15·5°
Tiglic acid dibromide	0·94 at 16° 1·01 at 20°	6·06 at 8° 11·89 at 20°	72·99 at 14·5° 87·28 at 21·5°	45·26 at 3° 69·98 at 15·5°

The homogeneity of the angelic acid dibromide was carefully tested by well shaking a weighed quantity of various samples of the compound with successive small quantities of water; the solubility remained absolutely constant, and not a trace of a crystalline powder (tiglic acid dibromide) could be detected in the small quantity of oil remaining undissolved after many treatments (compare Fittig, *loc. cit.*); this oil dissolved on adding sufficient water, the total quantity of water used being rather more than that calculated from the solubility of angelic acid dibromide.

When a mixture of the two dibromides is repeatedly extracted with successive small quantities of water, the angelic acid dibromide first passes into solution, its solubility, determined experimentally, being practically the same as when the pure substance alone is used; after about six extractions, under the conditions employed, the oily residue solidifies, and the extracts then contain tiglic acid dibromide in quantities corresponding very closely with those calculated from the normal solubility.

The solubility of the angelic acid dibromide is, however, slightly diminished by the presence of tiglic acid dibromide; when a saturated aqueous solution of pure angelic acid dibromide is shaken with a relatively very small quantity of tiglic acid dibromide, the latter first

becomes pasty and then changes to a turbid oil, owing to the separation of a small quantity of oily angelic acid dibromide.

The solubility of tiglic acid dibromide is diminished to an even greater extent by the presence of angelic acid dibromide, more than five-sixths of the compound being precipitated from its saturated aqueous solution as a crystalline powder on adding angelic acid dibromide to saturation, and then shaking well.

A further difference in the behaviour of the two dibromides is observed when they are triturated with tiglic acid in absence of moisture; the angelic acid dibromide forms an oily mixture with the tiglic acid, whereas the tiglic acid dibromide gives a powdery mixture; both the dibromides give an oily mixture when triturated with angelic acid.

Crystallographic measurements of the two dibromides, made by Fock with crystals obtained from petroleum pentane solution, showed slight but distinct differences between the two compounds.

When the above-mentioned normal conditions under which angelic acid is converted into its dibromide are not strictly adhered to, a considerable quantity of tiglic acid dibromide is formed; this compound may, in fact, be produced in such large quantities that a careless examination would lead to the conclusion that it was the sole product.

Numerous experiments were made in order to determine the influence of temperature, order of mixing, &c., on the course of the reaction.

In the first place, it was found that at temperatures above 25°, other conditions remaining normal, a considerable quantity of tiglic acid dibromide is formed; at 25—29°, of every 100 parts of angelic acid, at the most 14·5 parts are converted into tiglic acid dibromide; at 35—40°, about 28 parts. Tiglic acid dibromide is also formed when the carbon bisulphide solution of the bromine is added to that of the angelic acid, instead of *vice versâ*, other conditions remaining normal; at 16—20°, of every 100 parts of angelic acid about 35·9 parts are converted into tiglic acid dibromide; at 25—29°, about 46·7, and at 34—40°, about 68·7 parts.

The influence of bright light and of the order of mixing, on the course of the reaction are even more striking. When a carbon bisulphide solution of bromine in slight excess is slowly added in small quantities at a time to a carbon bisulphide solution of angelic acid, kept below 5°, but exposed to bright sunlight, each addition of bromine, except the last two, being made only after the solution has become colourless, the yield of tiglic acid dibromide varies from 88·74 to 92·8 per cent. of the crude brominated product, seemingly according to the intensity of the light; when, on the other hand, the solution of the acid is added to that of the bromine, the temperature remaining the same, the yield of tiglic acid dibromide is only 47·6 per cent. of the crude product, even when the operation is carried out in sunlight.

It is clear, therefore, that the principal cause to which the formation of tiglic acid dibromide is due must be active during and not after the combination of the angelic acid with the halogen; special

experiments showed that angelic acid dibromide is not transformed into the isomeride when its saturated solution in petroleum pentane is heated at 50°, or exposed for a long time to direct sunlight.

When tiglic acid is treated with bromine under the normal conditions, the product is invariably pure tiglic acid dibromide; when, however, the temperature is 25—29°, a small quantity (about 1·35 per cent.) of the crude product consists of angelic acid dibromide. The effect of adding the carbon bisulphide solution of the acid to that of the bromine is much more marked; at 18—20°, of every 100 parts of tiglic acid 3·77 parts, and at 43—45°, 7·94 parts, are converted into angelic acid dibromide when the reaction takes place in a very dim light; whereas in sunlight, even at 0°, the quantity of angelic acid dibromide varies from 7·43 to 11·58 per cent. of the mixed products, seemingly according to the intensity of the light.

In most of Fittig's experiments, it is definitely stated that the carbon bisulphide solution of bromine was added to that of the acid; and in all cases, with one exception, conditions favourable to the production of tiglic acid dibromide were dominant. In the exceptional case referred to, working by gaslight, the carbon bisulphide solution of the angelic acid was very slowly added to that of excess of bromine; as the next morning the solution was still deeply coloured with bromine, the mixture, cooled all the time in ice-water, was kept for three days exposed to diffused sunlight. Under these conditions, it was stated, the weight of pure tiglic acid dibromide isolated amounted to more than half that of the crude brominated product.

As this result was at variance with the author's observations, he repeated the experiment under exactly the same conditions as those employed by Fittig; it was found that the quantity of tiglic acid dibromide formed is certainly not as much as 5 per cent. of the crude brominated product.

The explanation of Fittig's results is to be sought for in the following facts:—Firstly, he used only a slight excess of bromine; secondly, the solutions were not only mixed at a low temperature, but were also kept at a low temperature over night; thirdly, the next morning the solutions were exposed to diffused, moderately bright sunlight. The first two conditions retard combination to such an extent that, even after keeping over night, the solution still contains angelic acid, which, on exposing the mixture to diffused sunlight, combines with the bromine present in only slight excess to form tiglic acid dibromide.

Although, it is true, Fittig worked under conditions favourable to the formation of tiglic acid dibromide, his statements relative to the yield of this compound are very untrustworthy; a sample of Fittig's own preparation, stated to consist essentially of tiglic acid dibromide, was examined by the author and found to contain 81·75 per cent. of angelic acid dibromide, and only 18·25 per cent. of the isomeride; a sample stated to be pure tiglic acid dibromide was found to contain as much as 25·57 per cent. of angelic acid dibromide.

Another fact which vitiated Fittig's results is, that he distilled the angelic acid employed in the bromination experiments; when pure

angelic acid (8—10 grams) is quickly distilled, more than 1·5 per cent. is converted into tiglic acid.

The sample of angelic acid dibromide prepared by Pückert, which, according to Fittig, contained calcium and "was wanting in all the properties of a pure compound" (*loc. cit.*) was carefully examined; it was found to contain calcium equivalent to 0·5 per cent. of calcium chloride, or 2·5 per cent. of the calcium salt of angelic acid dibromide, that is to say, a quantity too small to appreciably affect Pückert's analytical results. Two fresh samples of angelic acid dibromide were prepared, exactly as described by Pückert; they were found to contain only about 10 per cent. of tiglic acid dibromide, so that the sample examined by Fittig certainly could not have consisted principally of this compound, as was stated to be the case.

The bye-product obtained by Fittig in the preparation of angelic acid dibromide (*loc. cit.*), which was stated to have great influence on the properties of the tiglic acid dibromide, is an oily mixture or compound of angelic acid dibromide with angelic acid or tiglic acid (see above), and is formed in larger quantity the dimmer the light and the smaller the quantity of bromine used; when only 2 mols. of bromine are employed to 3 mols. of the acid, the experiment being carried out in a dim light, hardly any crystalline product is obtained; working in a bright light, solid mixtures consisting essentially of tiglic acid dibromide and tiglic acid are obtained, the angelic acid, under these conditions, being converted into the isomeride.

In order to investigate the nature of the bye-products formed in the preparation of angelic acid dibromide under the normal conditions, a large quantity (200 grams) of the pure acid was treated at various times in the normal manner; after separating the pure angelic acid dibromide as completely as possible, an operation which lasted about a year, nearly 11 grams of an oil, which appeared still to contain not inconsiderable quantities of angelic acid dibromide, remained. On treating this oil with sodium carbonate, about 1 gram of a coloured, neutral liquid containing bromine, probably a polymeride of bromobutylene, remained undissolved; the solution, on distillation, gave 1·65 grams of bromobutylene, a quantity equivalent to 3·1 grams of angelic acid dibromide, and from the residue about 0·2 gram of tiglic acid was isolated. The quantity of substance unaccounted for amounted therefore to little more than 0·67 per cent. of the crude bromination product, and may doubtless be put down as unavoidable loss incurred in the examination of the oil.

These experiments prove that a readily soluble substance, which, according to Fittig, has, even when present in very small quantities, a remarkable influence on the properties of tiglic acid dibromide, is not formed by the action of bromine on angelic acid.

Although it is impossible to fulfil Fittig's request, to submit to him a pure isomeride of tiglic acid dibromide "which passes into tiglic acid dibromide when its cold, freshly prepared solution is kept in a desiccator," the author considers that his present work has shown the existence and established the properties of angelic acid dibromide with as great a degree of certainty as has been done in the case of any other organic compound.

The reason that Pückert first observed the existence of this isomeride of tiglic acid dibromide, and that its discovery was not made years ago in Fittig's laboratory, is simply the result of accidental circumstances. In the Leipzig laboratory the draught cupboards happen to have been built between the windows, and are only dimly lighted; in the Strasburg laboratory, on the other hand, they are placed in the windows and receive bright daylight. Had the former been constructed like the latter, it is probable that angelic acid dibromide would not yet have been discovered. F. S. K.

Constitution of Angelic and Tiglic acids. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **23**, 178—217; compare Abstr., 1892, 1304).—The alcohol (b. p. 131—133°) from "mixed amylene" yields, on oxidation with dilute potassium permanganate, acetic, propionic, and glyoxylic (?) aldehydes, and an unsaturated aldehyde C_5H_8O; formic, acetic, propionic, and glycollic acids, along with a non-volatile dihydroxy-acid $C_5H_{10}O_4$, and a non-volatile neutral substance $C_5H_{12}O_3$, which is pentenylglycerol. This glycerol, on oxidation in the same manner, gives acetic, propionic, and glyoxylic aldehydes, acetic acid, propionic acid, oxalic acid, and the dihydroxy-acid; on oxidation with chromic mixture, it yields fumaric, acetic, and propionic acids. The author considers that these results show the alcohol to consist of two isomerides $CH_2{:}CEt{\cdot}CH_2{\cdot}OH$ and $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, from the former of which are derived the aldehyde $CH_2{:}CEt{\cdot}CHO$, and the propaldehyde. The dihydroxy-acid and the glycerol are probably mixtures of isomerides derived from both isomeric alcohols. The aldehyde C_5H_8O gives an acid $C_5H_8O_2$, probably α-ethoxyacrylic acid, which, when heated with sulphuric acid for 10 hours in a sealed tube at 100° is converted into tiglic acid.

Amongst the products of oxidation of angelic acid by potassium permanganate were found citramalic acid and glycollaldehyde. No glyceric acid was found amongst the oxidation products of tiglic acid. The author draws the conclusion that angelic acid is not α-ethylacrylic acid, but α-methylisocrotonic acid, and that the isomerism between angelic and tiglic acids is occasioned by a structural difference between them, and is not a case of geometrical isomerism. J. W.

Constitution of Glyoxylic acid. By R. OTTO and J. TRÖGER (*Ber.*, **25**, 3425—3429).—When potassium glyoxylate is added by degrees to a large excess of thiophenol, through which a steady current of hydrogen chloride is being passed, *dithiophenylacetic acid*, $COOH{\cdot}CH(SPh)_2$, is formed with development of heat. It forms faintly yellowish prisms (probably monosymmetric), melts at 104—106°, and is readily soluble in alcohol and ether, but insoluble in water. In the light of the experiments of Baumann and his pupils, on the formation of mercaptals from aldehydes and mercaptans, this result serves to show that glyoxylic acid is to be regarded as formylcarboxylic acid, COH·COOH, and not as dihydroxyacetic acid. Diphenylsulphonemethane (Fromm, Abstr., 1890, 56) is obtained when dithiophenylacetic acid is treated with potassium permanganate

solution and a few drops of dilute sulphuric acid in the presence of benzene. The authors find that this compound melts at 120—121°.

A. R. L.

Dibromosuccinic acids. By W. Lossen (*Annalen*, **272**, 127—139).—When dibromosuccinic acid is boiled for about 10 minutes with normal soda or potash, it is almost completely converted into the corresponding salt of acetylenedicarboxylic acid, with formation of sodium or potassium bromide; when more concentrated (about 12½ per cent.) soda is used, part of the sodium acetylenedicarboxylate undergoes decomposition into sodium propargylate and sodium carbonate with evolution of carbonic anhydride.

Dibromosuccinic acid is also decomposed by normal soda at the ordinary temperature, by boiling normal barium hydroxide, and by boiling milk of lime, the principal product being a salt of acetylenedicarboxylic acid in all cases; in one experiment, oxalic acid seemed to be formed in very small quantities when milk of lime was used.

Isodibromosuccinic acid behaves like dibromosuccinic acid towards boiling normal soda and boiling milk of lime, but is rather more readily decomposed.

Tartaric acid is not formed from either of the above mentioned acids under the conditions stated.

F. S. K.

Action of Sodium Ethoxide on Ethyl Dibromosuccinate. By A. Michael and C. C. Maisch (*J. pr. Chem.*, [2], **46**, 233—235).—Pim (Abstr., 1888, 1058) stated that the product of this reaction is ethyl acetylenedicarboxylate (this vol., i, 145). The authors find, however, that the product boils at 149—149·5° (20 mm.; temp. of bath 180°) and is destitute of the penetrating odour characteristic of ethyl acetylenedicarboxylate; they deduce, from their analyses of the compound, that it is ethyl diethoxysuccinate.

A. G. B.

Addition of Chlorine to Polybasic Unsaturated Fatty Acids. By A. Michael and G. Tissot (*J. pr. Chem.* [2], **46**, 381—399; compare this vol., i, 134).—When a 10 per cent. solution of chlorine in carbon tetrachloride acts on a solution of dimethylmaleïc anhydride in the same solvent for three days in a good light, a quantitative yield of α-dichloro-symmetrical-dimethylsuccinic anhydride (Abstr., 1890, 957) is obtained; it has a tear-exciting odour, is easily soluble in most solvents, and melts, with sublimation, at 159—160°. Its identity is settled by its easy conversion by water into the corresponding dichloradipic acid (Abstr., 1885, 753).

Citradichloropyrotartaric acid is formed when chlorine acts on citraconic anhydride in carbon tetrachloride in sunlight, and the product is treated with water. It crystallises, melts at 119—120° with decomposition, and dissolves in alcohol, ether, acetone, and ethyl acetate. By destructive distillation, it is split up into chlorocitraconic anhydride, hydrogen chloride, and water. When the acid is heated with water, carbonic anhydride, propaldehyde, chloromethylacrylic acid (m. p. 59°), chlorocitraconic anhydride (m. p.

98°—100), and chlorocitramalic acid (m. p. 139°) can be isolated from the solution. The *barium* (with 4 mols. H_2O) and *lead* (with 4 mols. H_2O) chlorocitramalates were prepared. Swarts (*Jahresber.*, 1873, 582) claimed to have prepared citradichloropyrotartaric acid by the action of chlorine on an aqueous solution of citraconic anhydride in sunlight; in view of the ease with which the acid is decomposed by water, this does not seem possible.

Chloromesaconic acid can be prepared by acting on citradichloropyrotartaric acid with alkalis. It crystallises in rhombic tables, sublimes gradually at 150°, melts at 208°, solidifies again at 200°, and dissolves in water, but only sparingly in benzene and chloroform. The *silver* and *barium* (with 4 mols. H_2O) salts were prepared.

Mesadichloropyrotartaric acid is obtained as its *chloride*, $C_5H_6Cl_4O_2$, (b. p. 105—106° at 21 mm.) when mesaconic chloride is treated with chlorine in carbon tetrachloride in sunlight; the chloride is decomposed by water and the acid isolated by extraction with ether. It crystallises in microscopic prisms, melts at 123°, and is less hygroscopic than the citra-acid. With water and alkalis, it behaves like the citra-acid, but is rather more easily decomposed by the former.

Allo-αβ-dichlorosuccinic anhydride is the product of the action of chlorine on maleïc anhydride in carbon tetrachloride in sunlight; it forms silvery crystals, melts at 95°, and is very hygroscopic, readily passing into the corresponding *acid*, which crystallises in large, transparent crystals, and melts at 175° with decomposition; when heated with water it passes into chlorofumaric acid (m. p. 190—191°).

αβ-Dichlorosuccinic chloride is similarly produced from fumaric chloride; it is a thick, colourless oil having a tear-exciting odour, and boils at 105—106° (45 mm.). By the prolonged action of water, it is converted into the corresponding *acid*, which crystallises in colourless prisms, melts at 215°, and is less soluble in water than the allo-acid; by alkalis it is converted into chlorofumaric acid, together with a small quantity of an acid of lower melting point, probably chloromaleïc acid.

In conclusion, the authors compare the above results with the decomposition of the corresponding bromo-acids by water as worked out by Fittig and Krusemark (*Annalen*, **206**, 1), who did not obtain bromomethylacrylic acid from citradibromopyrotartaric acid. How this affects the Michael-Wislicenus controversy is briefly discussed.

A. G. B.

Action of Chlorides of Bibasic Acids on Ethyl Sodiocyanacetate. By T. Mulder (*Compt. rend.*, **115**, 953—955).—On evaporating the ether used in washing the ethyl succinocyanacetate obtained by the action of succinic chloride on ethyl sodiocyanacetate, a yellowish substance is left, consisting of a mixture of ethyl cyanacetate and ethyl succinodicyanacetate, from which the latter may then be separated.

Ethyl succinodicyanacetate, $C_2H_4[CO\cdot CH(CN)\cdot COOEt]_2$, crystallises in small tufts of slender, white needles, and melts at 135—136°. It is hydrolysed by boiling water into succinic acid and ethyl cyan-

acetate, and is a true acid, decomposing alkaline carbonates. The *sodium*, *silver*, and *cuprous* salts are described. JN. W.

Addition of Bromine to Acetylenedicarboxylic acid and its Ethyl Salt. By A. MICHAEL (*J. pr. Chem.* [2], **46**, 210—233).—Bandrowski (Abstr., 1880, 160) found that dibromofumaric acid is the chief product of the action of bromine on acetylenedicarboxylic acid. This observation did not fall in with Wislicenus' theory as to the arrangement of atoms in space (Abstr., 1888, 1058), so that this chemist further investigated the reaction, and has stated (*Annalen*, **259**, 78) that, if the action of hydrogen bromide be excluded, dibromomaleïc acid is mainly produced. The author has shown (*J. pr. Chem.* [2], **37**, 34) that all acetylene derivatives formed by the displacement of the acetylene hydrogen by two negative organic radicles yield two alloisomeric dibromo-additive products; the present research proves that the dicarboxylic acid is no exception to this rule. Acetylenedicarboxylic acid melts at 178—179° (not 175°), and reacts rapidly with bromine in aqueous solution when exposed to bright diffused light, without the vigorous evolution of carbonic anhydride and formation of oily drops (bromoform, according to Bandrowski) noticed by the aforesaid observers. The separation of the products of the reaction was effected by means of lead acetate; lead bromofumarate dissolves in 993 parts of water at 20°; lead dibromofumarate dissolves in 92 parts of water at 17°; lead dibromomaleate dissolves in 721 parts of water at 17°. When precipitated by the addition of lead acetate to the aqueous solution of the corresponding acid, the solubility of these salts is modified by the presence of the acetic acid. On the addition of a 10 per cent. solution of lead acetate, 1 part of bromofumaric acid in 350 parts of water will still give an immediate precipitate of aggregates of crystals; 1 part of dibromomaleïc acid in 400 of water gives an immediate precipitate of specifically light needles; 1 part of bromomaleïc acid in 400 parts of water gives an amorphous precipitate, whilst 1 part of dibromofumaric acid in 10 parts of water gives no precipitate even after several days.

The results of six experiments, in which mixtures of 1 gram of acetylenedicarboxylic acid and 1·4 gram of bromine with varying quantities of water were exposed to sunshine, bright diffused daylight, and dull diffused daylight, show that even in the presence of hydrobromic acid some 70 per cent. of the product consists of dibromofumaric acid and some 30 per cent. of dibromomaleïc acid. The bromine content of the latter indicated that it was very nearly free from bromomaleïc and bromofumaric acids, which might accompany it by the lead acetate precipitation method. The melting point of dibromofumaric acid is 227°.

To prove that Wislicenus is wrong in supposing that bromomaleïc acid is the first product of the reaction, and that this is subsequently converted into bromofumaric acid by the hydrogen bromide formed by secondary reactions, the author submitted both acetylenedicarboxylic and bromomaleïc acids to the action of hydrobromic acid under similar conditions, at the ordinary temperature, with the result that whilst much bromofumaric acid was formed from the acetylenedi-

carboxylic acid, the bromomaleïc acid remained unchanged. If Wislicenus' views be correct, tribromosuccinic acid should yield dibromofumaric acid by the elimination of hydrogen bromide, but when this is effected by the careful addition of aqueous potassium hydroxide to a well-cooled solution of the acid, much dibromomaleïc acid is produced, but practically no dibromofumaric acid.

Ethyl acetylenedicarboxylate, $C_2(COOEt)_2$ (compare Abstr., 1888, 1058), is a colourless liquid which boils with decomposition under the ordinary pressure, but distils without decomposition at 120—121° under 20 mm. pressure. It has a tear-exciting odour.

This salt was dissolved in varying quantities of carbon tetrachloride; the solutions were cooled to −17°, exposed to sunlight, and the calculated quantity of bromine, also dissolved in carbon tetrachloride, was gradually added to them. The reaction is one of the most facile in organic chemistry; only traces of hydrogen bromide are formed, showing the absence of secondary reactions. Three experiments gave, respectively, 74·9, 74·3, and 72·9 per cent. of ethyl dibromofumarate, contaminated with only very little bromofumarate and bromomaleate, and 25·1, 25·7, and 27·1 per cent. of ethyl dibromomaleate.

Ethyl dibromofumarate, $C_2Br_2(COOEt)_2$, forms large, colourless, lustrous prisms with oblique terminal planes; it melts at 67—68°, and is insoluble in water, but soluble in cold chloroform, benzene, acetone, and hot light petroleum. *Ethyl dibromomaleate* is a colourless oil which boils at 162—164° (20 mm.).

When an ethereal solution of ethyl dibromofumarate is heated with zinc in a sealed tube at 60—70°, a good yield of ethyl acetylenedicarboxylate is obtained. This reaction ought not to occur, according to the Van't Hoff-Wislicenus hypothesis (compare Abstr., 1891, 1184; 1888, 1147). A. G. B.

Comparison of Experimental Results with the Theoretical Conclusions of the Van't Hoff-Wislicenus Hypothesis. By A. Michael (*J. pr. Chem.* [2], **46**, 400—424 and 424—427).—The experimental results referred to are those which have been recently published by Michael and his pupils, and a few earlier results obtained by others. A table showing 46 reactions, the results which these should give according to the Van't Hoff-Wislicenus hypothesis, the actual results, and references to the publications in which the experiments are detailed, are given. A. G. B.

Synthesis of Isomalic acid. By K. Brunner (*Monatsh.*, **13**, 834—839).—Hübner (*Annalen*, **120**, 334; **124**, 318) and Kleemann (Abstr., 1885, 505) both state that diacetyl cyanide, when treated with hydrochloric acid, is converted into hydrocyanic and acetic acids. The author finds that when it is treated at 0° with a solution of hydrogen chloride saturated at 0°, and after 24 hours the mixture is diluted with water, and the whole digested for some hours, isomalic and acetic acids are produced. The isomalic acid is identical with that described by Schmöger (Abstr., 1879, 618; 1882, 40). An improved method of preparing diacetyl cyanide is described. L. T. T.

Homologues of Malic acid. By A. Michaël and G. Tissot (*J. pr. Chem.* [2], **46**, 285—304; compare Abstr., 1891, 1455).—To prepare β-hydroxypyrotartaric acid, potassium cyanide is mixed with ethyl acetoacetate in ethereal solution, and treated with hydrochloric acid. After two weeks, the ethereal layer is evaporated, and the residue digested with hydrochloric acid for 6—8 hours, and again dried. The acid is extracted from this residue by dry ethyl acetate. It is indistinguishable from citramalic acid, both in its own physical properties and those of its salts. The *ammonium* salt forms microscopic, hygroscopic prisms, melts at 145°, and decomposes at 155—160°. The silver salt crystallises in needles, and is anhydrous (compare Morris, Trans., 1880, 10). When the acid is heated a little above its melting point, it is converted into citraconic anhydride and water. Morawski's citramalic acid was found to be identical with the acid just described. The identity of the two acids throws doubt on Morawski's statement that hydrochloroxycitraconic acid yields citramalic acid when reduced (this Journal, 1875, 1254); his experiment was therefore repeated, zinc being used as the reducing agent. The *methylmalic acid* obtained crystallises from ethyl acetate in white prisms, and melts at 123° (compare Wislicenus, Abstr., 1892, 589); its *calcium* salt (with 3 mols. H_2O), *lead* salt (with 1 mol. H_2O), and *zinc* salt are described.

αβ-Dimethylmalic acid was prepared by substituting methyl ethylacetoacetate for ethyl acetoacetate in the prescription for preparing β-hydroxypyrotartaric acid. It crystallises in small, colourless prisms, melts at 143°, is very slightly hygroscopic, and dissolves in most solvents except light petroleum. The *silver* (with $\frac{1}{2}$ mol. H_2O), *barium* (with 2 mols. H_2O), and *calcium* (with $4\frac{1}{2}$ mols. H_2O) salts have been obtained. When the acid is heated at 175°, it yields dimethylmaleïc anhydride (m. p. 96°).

α₂β-Hydroxymethylethylsuccinic acid (symmetrical ethylmethylmalic acid, Abstr., 1891, 1455) melts at 131·5—132°; the *ammonium* salt melts at 179°; the *silver* and *zinc* (with 4 mols. H_2O) salts were also prepared. The anhydride obtained by heating it, boils at 236—237° at ordinary pressure (not 226°, *loc. cit.*); the ammonium salt of the corresponding acid melts at 112°.

The behaviour of ethyl acetosuccinate with hydrocyanic acid is still being investigated (compare *loc. cit.*). A. G. B.

Ethyl Oxalacetate. By W. Wislicenus and A. Jensen (*Ber.*, **25**, 3448—3456).—Ethyl oxalacetate reacts with aldehydes in the same manner as does ethyl acetoacetate (Claisen and Matthews, *Annalen*, **218**, 270). When a mixture of ethyl oxalacetate and benzaldehyde in molecular proportion is saturated in the cold with dry hydrogen chloride, and allowed to remain in a closed vessel for some days, *ethyl benzylidenoxalacetic acid*, having most probably the constitution $COOH{\cdot}CO(CHPh){\cdot}COOEt$, separates. It crystallises in small, lustrous, felted needles, melts at 104—105°, distils partially undecomposed, under diminished pressure, and is readily soluble in alcohol and ether, but only sparingly in hot water. The *copper* salt, $C_{13}H_{11}O_5Cu$, is obtained as an oil, but subsequently solidifies; it crystallises from methyl alcohol

with 2 mols. of the solvent in rhombic plates melting at 117—119°. After eliminating the methyl alcohol by heating the salt in a toluene bath, it melts at 145° with decomposition. When the salt is distilled under diminished pressure, ethyl cinnamate passes over. The *phenylhydrazine* salt, $C_{19}H_{20}N_2O_5$, is formed by adding the calculated quantity of phenylhydrazine to a solution of the acid ethyl salt in dilute alcohol. It crystallises in stellate groups of needles, melts at 99°, and is readily converted into the *osazone* with the loss of water.

The *monhydrazone* of dihydroxytartaric acid, $C_{14}H_{16}N_2O_5$, is obtained in accordance with R. Meyer's views (*Annalen*, **247**, 190) when ethyl oxalacetate, dissolved in aqueous potash, is treated with diazobenzene chloride; it forms long, yellow needles, melts at 72—73° with the evolution of gas, and is readily soluble in ether, chloroform, and aqueous alkalis, but insoluble in water. Its yellow solution in concentrated sulphuric acid is coloured deep violet by potassium dichromate. If the compound is dissolved in alcohol and treated with phenylhydrazine, the osazone obtained by Anschütz and Geldermann (Abstr., 1891, 725) from ethyl dihydroxytartrate is formed, and when this is boiled with glacial acetic acid, it is converted into ethyl phenylhydrazoneketophenylpyrazolonecarboxylate (Wislicenus and Scheidt, Abstr., 1892, 458).

When an alkaline solution of diazobenzene chloride (2 mols.) is quickly added to one of ethyl oxalacetate (1 mol.), ethyl formazylcarboxylate, described by v. Pechmann (this vol., i, 82), and also by Bamberger and Wheelwright (*ibid.*, 84), is obtained. It agrees with the descriptions of these chemists, and when rapidly heated, melts at 113—114°; it also gives, on hydrolysis with alcoholic potash, an acid identical with that of v. Pechmann and Bamberger (*loc. cit.*).

A. R. L.

Optical Isomerides of d.-Mannoheptonic acid, d.-Mannoheptose, and Perseïtol. By W. S. Smith (*Annalen*, **272**, 182—190).—The compounds described below have been obtained from l.-mannose by the same methods as those employed in preparing the corresponding compounds of the d.-series (compare Fischer and Passmore, Abstr., 1890, 1230); the inactive substances were obtained by combining the members of the two optically active series in the usual way, but in many cases it could not be ascertained with certainty whether these products are the true racemic modifications or simply mixtures.

l.-Mannoheptonic acid was isolated in the form of its crystalline *barium* salt, $(C_7H_{13}O_8)_2Ba$. The *lactone*, $C_7H_{12}O_7$, separates from alcohol in crystals, melts at 153—155°, and has a specific rotatory power $[\alpha]_{D\infty}$ +75·15° in aqueous solution. The *hydrazide*, $C_7H_{13}O_7{\cdot}N_2H_2Ph$, separates from hot water in crystals, and melts at about 220° with decomposition when quickly heated.

i.-Mannoheptonic acid was obtained in the form of the *lactone*, $C_7H_{12}O_7$; this substance crystallises in small needles, melts at about 85°, has a sweet taste, and is rather more sparingly soluble in water than the two active lactones. The *calcium* salt, $(C_7H_{13}O_8)_2Ca + H_2O$, prepared from the lactone, crystallises from water in small, quadratic prisms, and loses its water at 110°. The *hydrazide*, $C_{13}H_{20}N_2O_7$, crys-

tallises from water in microscopic needles, and melts at 225° with decomposition.

l.-Mannoheptose is a colourless, deliquescent powder, and seems not to ferment with yeast. Its *hydrazone* crystallises from hot water in slender, colourless needles melting at about 196° with decomposition. Its *osazone*, $C_7H_{12}O_5(N_2HPh)_2$, crystallises from hot alcohol in slender needles and melts at about 203° with decomposition.

i.-Mannoheptose is a colourless syrup, only sparingly soluble in alcohol, and does not ferment with yeast. The *hydrazone* melts at 175—177° with decomposition. The *osazone*, $C_7H_{12}O_5(N_2HPh)_2$, crystallises in yellow needles, and melts at about 210° with decomposition.

l.-Mannoheptitol, $C_7H_{16}O_7$, separates from hot methyl alcohol and from hot water in crystals, and melts at 187° (corr.).

i.-Mannoheptitol, $C_7H_{16}O_7$, crystallises from water in microscopic plates, and melts at 203° (corr.). F. S. K.

Derivatives of d.-Mannoheptonic acid. By G. Hartmann (*Annalen*, **272**, 190—197).—Fischer has shown that two stereoisomeric acids are usually formed by the hydrolysis of the product of the combination of a sugar with hydrogen cyanide; the author's experiments prove that the acid obtained in this way from d.-mannose (Abstr., 1890, 1230), in quantities amounting to 87·4 per cent. of the theoretical, is not a mixture, and that the stereochemical isomeride is not produced in the reaction in question.

Calcium d.-mannoheptonate, $(C_7H_{13}O_8)_2Ca$, is soluble in about 30 parts of hot water, from which it crystallises in slender needles; the *strontium* salt, $(C_7H_{13}O_8)_2Sr$, is a semi-crystalline compound, much more readily soluble in water. The *cadmium* salt, $(C_7H_{13}O_8)_2Cd$, crystallises in well-defined needles, and is soluble in about 100 parts of boiling water.

Attempts to resolve d.-mannoheptonic acid into two stereochemical isomerides by means of its strychnine and brucine salts were unsuccessful; the *brucine* salt, $C_7H_{14}O_8,C_{23}H_{26}N_2O_4$, separates from hot 90 per cent. alcohol in well-defined crystals, melts at 161°, and seems to contain water of crystallisation.

Pentahydroxypimelic acid, $COOH\cdot[CH\cdot OH]_5\cdot COOH$, is formed when d.-mannoheptonic acid is oxidised with nitric acid of sp. gr. 1·2 at 45—50°; when purified by means of its calcium salt, it is obtained as a yellow syrup, very readily soluble in water and alcohol, the aqueous solution being lævo-rotatory. The *calcium* salt, $C_7H_{10}O_9Ca + 4H_2O$, separates from hot water in the form of a crystalline powder; it loses its water at 108°, and is only sparingly soluble in hot water. The *ethyl* salt, $C_{11}H_{20}O_9$, is formed when the acid is repeatedly evaporated with alcohol; it crystallises from hot alcohol in colourless needles, melts at 166°, and is readily soluble in water. The *dihydrazide*, $C_5H_{10}O_5(CO\cdot N_2H_2Ph)_2$, crystallises in yellowish plates, and melts at about 225° with decomposition when quickly heated.

F. S. K.

Lactosecarboxylic acid and Maltosecarboxylic acid. By O. Reinbrecht (*Annalen*, **272**, 197—200).—*Lactosecarboxylic acid*,

$C_{12}H_{22}O_{11}$·COOH, can be prepared by treating lactose with hydrogen cyanide under the usual conditions, and hydrolysing the product with barium hydroxide; it is a colourless, vitreous substance, has a sour taste, and does not reduce Fehling's solution. Its *calcium*, *strontium*, and *barium* salts are amorphous and readily soluble. When the acid is warmed with dilute mineral acids, it is decomposed into galactose and α-glucoheptonic acid.

Maltosecarboxylic acid, prepared from maltose in a similar manner, resembles the preceding compound; on hydrolysis with mineral acids, it is decomposed into glucose and α-glucoheptonic acid.

F. S. K.

Hydurilic acid. By C. Matignon (*Compt. rend.*, **115**, 955—958).—Hydurilic acid, $C_8H_6N_4O_2$, forms monopotassium and dipotassium salts (compare Baeyer, *Annalen*, **127**, 14). The heat of neutralisation with 2 mols. of potash is 21·8 Cal., but on adding a further quantity (up to 16 mols.), 4·2 Cal. more is liberated, thus pointing to a third very feeble acid function. The heat of neutralisation for the *monopotassium* salt (3 mols. potash) is +7·8 Cal., so that the heat of formation of the salt (calculated for solids throughout) is +32·0 Cal. The *dipotassium salt*, with $3H_2O$, absorbs 4·2 Cal. when dissolved in potash (2 mols.), so that the value of the second acid function is +21·7 Cal.

Jn. W.

Aromatic Iodochlorides, Iodosobenzene, and Iodoxybenzene. By C. Willgerodt (*Ber.*, **25**, 3494—3502).—Iodochlorides are obtained by treating aromatic iodo-compounds dissolved in chloroform or carbon tetrachloride with chlorine (compare Abstr., 1886, 341).

Diiodobenzene tetrachloride, $C_6H_4I_2Cl_4$ or $C_6H_4(ICl_2)_2$, is a greenish-yellow powder, decomposes at 155—156°, and darkens on exposure to light and air.

Triiodobenzene hexachloride, $C_6H_3I_3Cl_6$ or $C_6H_3(ICl_2)_3$, decomposes at 145°.

Phenyl iodochloride, when exposed to damp air, becomes opaque, and decomposes with evolution of hydrogen chloride.

Orthiodophenol reacts with chlorine with evolution of hydrogen chloride, and, after a time, the liquid deposits a yellow, crystalline iodochloride, which soon decomposes with elimination of iodine.

Iodosobenzene, C_6H_5·IO, is obtained by treating phenyl iodochloride with an aqueous solution of potassium or sodium hydroxide. It is a yellow, amorphous compound, has a characteristic odour, explodes violently when heated to 210°, and yields phenyl iodochloride when treated with phosphorus pentachloride. It reacts explosively with aniline and picric acid, and oxidises formic acid to carbonic acid. With acids, it forms salts. The *acetate*, $IPh(OAc)_2$, crystallises in large, colourless prisms, melts at 156—157°, and is neutral to litmus. The benzene solution becomes acid on boiling. The *propionate* crystallises in colourless needles and prisms, and melts at 63—64°. The *normal butyrate* melts at 68—69°. The *hydrochloride* crystallises in long needles. The *nitrate*, $IPh(NO_3)_2$, obtained by dissolving iodosobenzene in dilute nitric acid, crystallises in large, greenish-yellow prisms, and decomposes at 105—106° with a feeble explosion.

Iodosobenzene also dissolves in hydrofluoric, fluosilicic, and sulphuric acids.

Iodoxybenzene, $C_6H_5{\cdot}IO_2$, is obtained by heating iodosobenzene at 90—100° in the air. It crystallises in white needles, explodes at 227—230°, and is neutral. It explodes when treated with phosphorus pentachloride or strong sulphuric acid. With aniline, it gives a blood-red coloration. With fuming nitric acid, it yields paranitriodobenzene (m. p. 165°). E. C. R.

Hydrogenation of Benzene. By N. KIJNER (*J. Russ. Chem. Soc.*, **23**, 20—26).—1 c.c. of pure benzene was sealed up in a tube with 25 c.c. of hydriodic acid of sp. gr. 1·96 and heated for 24 hours at 280°. The layer of hydrocarbon was separated, washed with a solution of alkali, distilled with steam, and dried with calcium chloride. 24 grams of the substance obtained in this way were fractionated, and yielded 18 grams distilling between 69° and 73°. The residue was again treated with fuming hydriodic acid, and the hydrocarbon from it began to boil at 71°, most of it passing over below 75°, but a small quantity of high boiling material remained, which only distilled above 170°. As this did not react with fuming nitric acid, it could only be a condensation product of fully hydrogenised benzene, and not of benzene itself. The sp. gr. of the chief fraction (69—73°) was 0·7838 at 0°, indicating the presence of unchanged benzene. In order to remove this admixture, the following process was adopted:—

Triphenylmethane was melted and mixed with the liquid. On cooling, it crystallised out, taking along with it a large proportion of the benzene. The liquid was poured off and again treated in the same way. On fractionation, it now passed over almost entirely between 68° and 70° at 751 mm., its sp. gr. being 0·7609 at 0°/0° and 0·7428 at 19·5°/0°. It still reacted feebly at 0° with fuming nitric acid, after treatment with which it was again dried and distilled. It now came over between 69° and 71° at 761 mm., and had the sp. gr. 0·7473 at 0°/0°. The numbers obtained on analysis, agreed well with the formula C_6H_{12}, although it is probable that the substance was not quite free from hexane.

Fuming sulphuric acid, if in great excess, dissolves hexahydrobenzene with slight development of heat, the acid becoming brown and giving off sulphurous anhydride.

Fuming nitric acid at 0° scarcely acts on hexahydrobenzene, but, if the mixture is not cooled, the hydrocarbon dissolves with disengagement of heat. No oil separates when the mixture is poured into water, and no smell of nitrobenzene can be detected. A mixture of nitric and sulphuric acids is also without nitrating effect.

Excess of bromine in presence of a small quantity of aluminium bromide gives with hexahydrobenzene, a crystalline compound, which, after recrystallisation from benzene, melts at 124—125°. The compound cannot, therefore, be hexabromobenzene, as Konovaloff's experiments would lead one to expect (*J. Russ. Chem. Soc.*, **11**, 146). J. W.

Sandmeyer's Reaction and Preparation of Orthochlorotoluene. By H. ERDMANN (*Annalen*, **272**, 141—147; compare Arm-

strong and Wynne, Proc., 1892, 199).—In discussing Sandmeyer's reaction, the author points out that it is the formation of phenols and of azo-compounds which diminishes the yield when the conditions are not suitably chosen. The production of a phenol is due to the decomposition of the diazo-compound before it has been converted into the cuprous chloride compound, this taking place more especially when the amido-compound is diazotised in too concentrated solution, or at too high a temperature, or without stirring well; also when the solution of the diazo-compound is added too slowly to the boiling cuprous chloride solution.

The normal decomposition of the diazo-cuprous chloride compound takes place rapidly and smoothly only above a certain temperature, which is different for each compound; these temperatures are about 0°, about 27°, about 30—40°, and about 40—50° in the case of the cuprous chloride derivatives of diazobenzene, orthodiazotoluene, paradiazotoluene, and paradiazochlorobenzaldehyde respectively. Below these particular temperatures, the evolution of nitrogen takes place too slowly, and is incomplete, part of the diazo-cuprous chloride compound being reduced to an azo-compound by the liberated cuprous chloride, which is then present in excess; the yield of pure azo-compound may sometimes amount to more than 10 per cent. of the base employed.

When the diazo-compound is very readily decomposed, as is that of orthotoluidine, for example, the amido-base should be diazotised in very dilute, well-cooled solution, and the product decomposed with cuprous chloride at a low temperature; under these conditions, the yield of pure orthochlorotoluene is 70 per cent. of the theoretical.

F. S. K.

Heptanaphthene from Caucasian Naphtha. By E. Spindler (*J. Russ. Chem. Soc.*, **23**, 40—44).—Milkoffsky isolated from Caucasian naphtha a hydrocarbon, C_7H_{14}, boiling at 100—101°, and having the properties of a saturated hydrocarbon. From this, he obtained a chlorinated compound, which he did not investigate further. The chloro-derivative boils at 157—159°, and has the composition $C_7H_{13}Cl$. If impure, it gives off small quantities of hydrogen chloride on being distilled, but the pure substance distils unchanged. Its sp. gr. at 0°/0° is 0·9769; at 20°/0°, 0·9589. From the chloride, the author prepared a heptanaphthylene, by heating 1 part of it with $1\frac{1}{2}$ parts of potassium acetate and a little strong acetic acid in a sealed tube at 210° for 11 hours. The contents of the tube were neutralised with alkali and distilled with steam; a layer lighter than water separated from the distillate, and this layer was washed, dried, and distilled. The chief portion boiled at 102—104°, a few drops between 110° and 180°, and about a fourth of the whole between 180° and 190°. The portion boiling between 102° and 104°, when analysed, yielded numbers agreeing with the formula C_7H_{12}. The sp. gr. of this heptanaphthylene is 0·8085 at 0°/0°, and 0·7910 at 20°/0°. It combines with hydrogen bromide at the ordinary temperature and at 100°, but not energetically, and a portion of the hydrocarbon always remains unattacked.

Heptanaphthene, when dropped into 12 times its weight of bromine in presence of aluminium bromide, reacts energetically at first, but the reaction soon moderates, and hydrogen bromide at last comes off only very slowly. A crystalline substance is formed, which, when freed from a slight admixture of an oil and recrystallised from benzene, melts at 282—283°. At a higher temperature, it volatilises, forming white needles in the cooler portions of the tube. Its composition corresponds with the formula $C_7H_3Br_5$, and the melting point indicates that it is pentabromotoluene.

It would thus appear that the heptanaphthene from Caucasian petroleum is hexahydrotoluene, the boiling point of the latter being, however, 97°, instead of 100—101°. J. W.

Hydrolysis of Phenolic Ethers and of Ethereal Salts by means of Aluminium Chloride. By C. HARTMANN and L. GATTERMANN (*Ber.*, **25**, 3531—3534).—Phenolic ethers are readily hydrolysed by the action of aluminium chloride; the method is also applicable to nitro- and ketonic compounds, which are reduced on treatment with hydriodic acid.

Methoxybenzene, ethoxybenzene, and isobutoxybenzene, respectively, are hydrolysed by heating for three hours at 120° with 1·5 parts of aluminium chloride.

With orthonitro-methoxy- or ethoxy-benzene, the reaction proceeds more energetically; the phenol (1 part) should be dissolved in an equal weight of carbon bisulphide, and treated with aluminium chloride (1 part). The yield is 90 per cent. of the theory.

Orthohydroxymethoxybenzene and orthomethoxyhydroxytoluene [1 : 3 : 4], on treatment with aluminium chloride at 210°, give orthodihydroxybenzene and orthodihydroxytoluene respectively; the yield is 70 per cent. of the theoretical.

Parahydroxyacetophenone is obtained by heating aluminium chloride with paracetylmethoxybenzene at 140°, or with paracetylethoxybenzene at 180°; the yield is 70 per cent.

Parahydroxybenzophenone and α-hydroxyacetonaphthalene may be prepared in a similar manner from aluminium chloride and benzoylmethoxybenzene, or α-ethoxyacetonaphthalene, by heating for 1½ hours at 200—210°.

Many ethereal salts are also hydrolysed by the action of aluminium chloride; the authors have experimented with the ethyl salts of the following acids: acetic, succinic, phthalic, cinnamic, and paranitrocinnamic, and also with methyl salicylate. J. B. T.

Propylamidophenol from Camphor. By P. CAZENEUVE (*Compt. rend.*, **115**, 825—827).—The nitroketone, $NO_2{\cdot}C_9H_{11}O$, obtained by the action of nitric acid on the sulphone derived from monochlorocamphor (Abstr., 1892, 999), when treated with tin and hydrochloric acid, yields an amidophenol, the ketonic group, $-CH_2{\cdot}CO-$, being converted into a phenolic group, $-C(OH):CH-$, by intramolecular migration at the time that the nitro-group is reduced. The product has the composition $NH_2{\cdot}C_6H_3Pr{\cdot}OH$, and is purified by precipitation by ammonia from the solution of its hydrochloride, and repeated

recrystallisation from benzene. The base forms lamellar crystals, composed of slender, microscopic needles, which melt at 122° with slight decomposition, and distil at 260° partially without decomposition; it is insoluble in water, but dissolves in alcohol, ether, and benzene, and is also soluble in acids and alkalis. The alkaline solutions oxidise very rapidly when exposed to air, and become brownish-yellow. The alcoholic solution of the base gives a wine-red coloration with ferric chloride; the aqueous solution of the hydrochloride gives an intense red coloration and a precipitate with the same reagent. The *acetyl* derivative is insoluble in alkalis, and gives no coloration with ferric chloride. The base forms a slightly soluble picrate, which crystallises in beautiful needles; a slightly soluble ferrocyanide, which is crystallisable, but slowly decomposes; and a maroon-coloured insoluble platinochloride, which is very readily oxidised. Hydroxylamine and phenylhydrazine are without action, but when the compound is heated with zinc-dust in a current of hydrogen, it yields a hydrocarbon, C_9H_{12}, which boils at 150—156°. Cumene boils at 151°, and propylbenzene at 157°.

When the base is treated with concentrated sulphuric acid and alcohol, and the theoretical quantity of an aqueous solution of an alkaline nitrite is added, a phenol is obtained, and hence it is clear that the phenol group pre-exists in the base. A solution of nitric acid in sulphuric acid gives a bright red coloration with solutions of the base.

From these results, it would seem that the new base is a propylamidophenol [$NH_2 : OH : Pr = 1 : 3 : 4$], and it follows that the fundamental nucleus of camphor is really paracymene, as the other reactions of camphor indicate. C. H. B.

Action of Thiocarbimides on Aromatic Hydrocarbons. By A. Friedmann and L. Gattermann (*Ber.*, **25**, 3525—3528).—Leuckart has shown (Abstr., 1885, 773, 1224) that phenyl cyanate unites with aromatic hydrocarbons in presence of aluminium chloride with formation of anilides, phenyl cyanate and benzene giving benzanilide, NHPh·COPh; he was unable, however, to carry out a similar reaction with the thiocarbimides, and the author had likewise since attempted the same reaction without success. A renewed attempt, in which pure aluminium chloride, prepared from aluminium and hydrogen chloride, was employed, has brought about the desired result.

To carry out the reaction, a mixture of phenylthiocarbimide and benzene is heated on the water-bath with pure aluminium chloride for 1½ hours, and then allowed to remain 24 hours, after which water is carefully added, and the mixture steam distilled. The product of the reaction separates from the residue on cooling, and consists of a mixture of two compounds, which can be separated by treatment with dilute alkali. The solution, when acidified, yields thiobenzanilide, NHPh·CSPh; whilst the residue, after treatment with alkali, has the composition $C_{14}H_{10}N_2S_2$, and can also be formed by the action of aluminium chloride on phenylthiocarbimide alone, phenylcarbamide being simultaneously produced; it crystallises from alcohol in pale-yellow,

lustrous needles melting at 154°. Its constitution is not yet exactly determined.

With aluminium chloride, phenylthiocarbimide and toluene yield thiotoluylanilide only, $NHPh{\cdot}CS{\cdot}C_6H_4Me$, which separates from alcohol in long, yellow needles melting at 140—141°; paratolylthiocarbimide and toluene yield, chiefly, the thioanilide, which melts at 165—166°; in the absence of toluene, a substance insoluble in alkali is formed, which separates from acetone in well-developed sulphur-yellow crystals, and melts at 175—176°. H. G. C.

Action of Phenol Ethers on Thiocarbimides. By K. Tust and L. Gattermann (*Ber.*, **25**, 3528—3530).—Phenol ethers, like hydrocarbons, react with thiocarbimides in presence of pure aluminium chloride, but the action proceeds much more smoothly. Anisoïl and phenylthiocarbimide yield the *thioanilide* of *anisic acid*, $NHPh{\cdot}CS{\cdot}C_6H_4{\cdot}OMe$, which separates from alcohol in yellow crystals melting at 153—154°. It readily undergoes oxidation on treatment with potassium ferricyanide, forming the compound

$$C_6H_4\!<\!\begin{matrix}S\\N\end{matrix}\!>\!C{\cdot}C_6H_4{\cdot}OMe\ ;$$

this crystallises from acetic acid in colourless needles, and melts at 134—135°. Phenetoïl and phenylthiocarbimide yield the corresponding thioanilide, $NHPh{\cdot}CS{\cdot}C_6H_4{\cdot}OEt$, which forms yellow needles melting at 143°, and on oxidation with ferricyanide is converted into the compound $C_6H_4\!<\!\begin{matrix}S\\N\end{matrix}\!>\!C{\cdot}C_6H_4{\cdot}OEt$. α-Naphthyl ethyl ether and phenylthiocarbimide yield the thioanilide, $NHPh{\cdot}CS{\cdot}C_{10}H_6{\cdot}OEt$, which crystallises from acetic acid in yellow needles, and melts at 199—200°. Other thioanilides of different phenol ethers have also been prepared by the same reaction. H. G. C.

Aromatic Diazo-compounds. By H. v. Pechmann (*Ber.*, **25**, 3505).—The author believes that paradiazotoluene exists in alkaline solution as a nitrosamine, $C_6H_4Me{\cdot}NH{\cdot}NO$, for when the alkaline solution is treated with benzoic chloride, a compound is obtained which is probably nitrosobenzotoluidide, $C_6H_4Me{\cdot}N(NO){\cdot}COPh$. This crystallises from acetone in colourless needles, is very unstable, explodes when heated, gives Liebermann's reaction, and when reduced with zinc-dust and acetic acid yields parabenzotoluidide (m. p. 157—158°). E. C. R.

Salts and Derivatives of Phenylhydrazine. By B. Thieme (*Annalen*, **272**, 209—213).—*Phenylhydrazine thiosulphate*,

$$(N_2PhH_3)_2,H_2S_2O_3,$$

crystallises in colourless plates, melts at about 113° with decomposition when quickly heated, and is insoluble in ether; when heated at 120—130° for a long time, it is completely decomposed, yielding nitrogen, ammonia, hydrogen sulphide, benzene, aniline, thiophenol, and diphenyl sulphide. The *sulphite*, $(N_2PhH_3)_2,H_2SO_3$, crystallises in small, colourless plates, and melts at about 94° with decomposition

when quickly heated. The nitrate, N_2PhH_3,HNO_3, melts at about 145° with decomposition. The *phosphate*, $(N_2PhH_3)_2,H_3PO_4$, prepared by mixing concentrated solutions of disodium hydrogen phosphate and phenylhydrazine acetate, forms small plates, and melts at about 155° with decomposition. The *hydrofluoride*, N_2PhH_3,HF, is formed when hydrogen fluoride is passed into an alcoholic solution of excess of the base; it melts at about 166—167° with decomposition. The acid *hydrofluoride*, $N_2PhH_3,2HF$, is produced when the normal salt is treated with alcohol; it forms slender needles, sublimes with partial decomposition, and is insoluble in ether.

A compound, which seems to have the composition $(N_2PhH_3)_2,P_2O_5$, is formed when an ethereal solution of phenylhydrazine is added to phosphoric anhydride; it melts at 242—248° with decomposition.

F. S. K.

Bromination of Phenylhydrazine. By P. Meyer (*Annalen*, 272, 214—220).—*Orthodibromophenylhydrazine* $[N_2H_3 : Br_2 = 1 : 3 : 4]$ can be prepared by brominating acetonephenylhydrazone in chloroform solution and decomposing, with soda, the hydrobromide obtained in this way; it crystallises from alcohol in moss-like needles, melts at 104°, and turns brown on exposure to the air. The *hydrochloride*, $C_6H_3Br_2{\cdot}N_2H_3,HCl$, crystallises in lustrous needles, melting just above 200° with decomposition. The *sulphate*,

$$(C_6H_3Br_2{\cdot}N_2H_3)_2,H_2SO_4,$$

is readily soluble in water, and crystallises in lustrous needles. The *nitrate* forms colourless needles, and melts at about 163° with decomposition. The *picrate*, $C_6H_3Br_2{\cdot}N_2H_3,C_6H_3N_3O_7$, melts at about 132° with decomposition. The *oxalate*, $(C_6H_3Br_2{\cdot}N_2H_3)_2,C_2H_2O_4$, crystallises in colourless plates melting at about 174° with decomposition. The *acetyl* derivative, $C_6H_3Br_2{\cdot}N_2H_2Ac$, separates from hot alcohol in long, colourless needles, and melts at about 162—163° with decomposition. The *benzylidene* derivative, $C_6H_3Br_2{\cdot}N_2H{:}CHPh$, crystallises from light petroleum in colourless needles, and melts at 123°. When orthodibromophenylhydrazine is reduced with zinc-dust and hydrochloric acid, it is converted into parabromaniline, $C_6H_4Br{\cdot}NH_2$.

Metadibromophenylhydrazine $[N_2H_3 : Br_2 = 1 : 2 : 4]$, prepared from metadibromaniline in the usual manner, crystallises in colourless, moss-like needles, melts at 91°, and decomposes at about 178°; the *hydrochloride* crystallises in long needles. The *acetyl* derivative, $C_6H_3Br_2{\cdot}N_2H_2Ac$, separates from alcohol in colourless prisms melting at 146°. When metadibromophenylhydrazine is reduced with zinc-dust and hydrochloric acid, it is converted into parabromaniline; the last-named compound is also obtained from metadibromaniline under the same conditions.

F. S. K.

Paranitrophenylhydrazine. By A. Purgotti (*Real. Accad. Linc.*, 7, ii, 266—270).—A mixture of paranitraniline, hydrochloric acid, and water is diazotised with a solution of sodium nitrite. The product is slowly poured into sodium hydrogen sulphite solution, cooled with ice, and subsequently heated on the water-bath at 70°, with occasional addition of sodium hydrogen sulphite, so that the solution always

has a strong odour of sulphurous anhydride. The reddish precipitate formed soon coagulates and is filtered off; after further evaporation of the filtrate, *sodium paranitrophenylhydrazinesulphonate*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N \cdot SO_3Na, 2H_2O,$$

separates. It forms minute, yellow crystals, which begin to decompose at 115—120°, and deflagrate on ignition; it is readily soluble in water, sparingly so in alcohol, and rapidly reduces silver nitrate and Fehling's solution. The *barium* salt forms yellowish, spherical, acicular aggregates, containing 1 mol. H_2O; it is sparingly soluble in hot water, decomposes above 180°, and is a strong reducing agent.

On heating the sodium salt with hydrochloric acid (sp. gr. 1·19), and cooling the solution, *paranitrophenylhydrazine*, $NO_2 \cdot C_6H_4 \cdot N_2H_3, HCl$, separates; it forms small, reddish crystals, and is sparingly soluble in alcohol. Its aqueous solution slowly decomposes on exposure to the air.

Paranitrophenylhydrazine is obtained by heating the aqueous solution of the hydrochloride with sodium acetate, the precipitate being crystallised from boiling alcohol. It forms small, brown scales or needles, and melts at 157° with evolution of gas; it is very soluble in hot alcohol, but only sparingly in cold alcohol or water, and insoluble in benzene. It reduces silver nitrate or Fehling's solution, and on boiling with benzaldehyde in alcoholic solution, yields reddish crystals, which melt at 190°; this substance is now under examination. W. J. P.

Synthesis of Formazyl Compounds by the Action of Diazobenzene on Hydrazones. By W. Wislicenus (*Ber.*, **25**, 3456—3458; compare this vol., i, 82).—Formazylphenyl separates when diazobenzene chloride is added to benzylidenehydrazone and sodium ethoxide; it melts at 167—168°, whereas v. Pechmann states that the melting point is "about 175°"; the disparity in the values may, however, be due to a difference in the manner of heating.

Diazobenzene chloride and glyoxylic hydrazone react in a similar way, forming formazylazobenzene, which v. Pechmann has obtained from mesoxalic hydrazone, and Bamberger from ethyl acetoacetate. A. R. L.

Action of Diazobenzene on β-Ketonic acids. By E. Bamberger (*Ber.*, **25**, 3547—3555; compare this vol., i, 84, and v. Pechmann, this vol., i, 82).—v. Pechmann's work on the interaction of diazobenzene and hydrazones of the formula $NHPh \cdot N{:}CXY$ has led him to the conclusion that, when X and Y represent hydrogen, carboxyl, carbethoxyl, or an acid radicle, they are eliminated in the form of their hydroxyl compounds, and are replaced by the group $NPh{:}N$. Whilst agreeing substantially with v. Pechmann's statement, the author finds no evidence to show that the carbethoxy- and benzoyl groups can be displaced by the diazobenzene radicle.

Ethyl acetoacetate, when treated with diazobenzene in alkaline solution, yields practically pure ethyl formazylcarboxylate, $NPh{:}N \cdot C(N \cdot NHPh) \cdot COOEt$.

By the action of acetoacetic acid on diazobenzene, pure phenylazoformazyl, $C(N{:}NPh)_2{:}N{\cdot}NHPh$, is formed.

Ethyl formazylcarboxylate is not acted on by diazobenzene in alkaline solution at 0°, but formazylcarboxylic acid, under the same conditions, is converted into phenylazoformazyl.

Ethyl benzoylacetate, on treatment with diazobenzene at 0°, yields ethyl phenylhydrazonebenzoylformate, $N_2HPh{:}CBz{\cdot}COOEt$. Benzoylacetic acid and diazobenzene give formazyl phenyl ketone,

$$N_2Ph{\cdot}CBz{:}N{\cdot}NHPh;$$

by the further action of diazobenzene on this substance, phenylazoformazyl appears to be formed in very small quantity; the greater part of the ketone is, however, recovered unchanged.

Ethyl acetoacetate and acetoacetic acid yield at least five compounds with diazobenzene, according to the experimental conditions; they are shown in the following table, together with other compounds formed from diazobenzene and various acids and ethereal salts. It will be seen that the hydrazone radicle is not always eliminated by the action of diazobenzene:—

Ethyl acetoacetate (1 mol.) and diazobenzene (1 mol.) give ethyl benzeneazoacetate, $COOEt{\cdot}CAc{:}N{\cdot}NHPh$.

Ethyl acetoacetate (1 mol.) and diazobenzene (2 or 3 mols.) in alkaline solution give ethyl formazylcarboxylate,

$$NPh{:}N{\cdot}C(N{\cdot}NHPh){\cdot}COOEt.$$

Acetoacetic acid (1 mol.) and diazobenzene (1 mol.) in acetic acid solution give pyruvic aldehyde hydrazone, $CHAc{:}N{\cdot}NHPh$, and formazyl methyl ketone, $N_2Ph{\cdot}CAc{:}N{\cdot}NHPh$.

Acetoacetic acid (1 mol.) and diazobenzene (2 mols.) in alkaline carbonate solution give formazyl methyl ketone.

Acetoacetic acid (1 mol.) and diazobenzene (3 mols.) in alkaline solution give phenylazoformazyl, $NHPh{\cdot}N{:}C(N{:}NPh)_2$.

Ethyl alkyl acetoacetate (1 mol.) and diazobenzene (1 mol.) give ethyl pyruvate hydrazone, $NHPh{\cdot}N{:}CMe{\cdot}COOEt$.

Alkylacetoacetic acid (1 mol.) and diazobenzene (1 mol.) give diacetylphenylhydrazone, $NHPh{\cdot}N{:}CMeAc$.

Alkylacetoacetic acid (1 mol.) and diazobenzene (2 mols.) give methylformazyl, $NHPh{\cdot}N{:}CMe{\cdot}N{:}NPh$.

Ethyl benzoylacetate (1 mol.) and diazobenzene (1 or 3 mols.) give ethyl benzoylglyoxalate hydrazone, $NHPh{\cdot}N{:}CBz{\cdot}COOEt$.

Benzoylacetic acid (1 mol.) and diazobenzene (1 mol.) give phenylglyoxalic hydrazone, $NHPh{\cdot}N{:}CHBz$, and formazyl phenyl ketone, $NHPh{\cdot}N{:}CBz{:}N{\cdot}NPh$.

Benzoylacetic acid (1 mol.) and diazobenzene (2 or 3 mols.) give formazyl phenyl ketone.

Ethyl hydrogen malonate hydrazone (1 mol.) and diazobenzene (1 mol.) give ethyl formazylcarboxylate, $NHPh{\cdot}N{:}C(N{:}NPh){\cdot}COOEt$.

J. B. T.

Formazyl Methyl Ketone. By E. Bamberger and J. Lorenzen (*Ber.*, **25**, 3539—3547; compare this vol., i, 84).—The constitution of formazyl methyl ketone is shown by its formation from benzeneazo-

acetoacetic acid and diazobenzene, whilst by the action of diazobenzene in presence of an alkali on the ketone, acetic acid and phenylazoformazyl are produced.

β-Phenotriazyl α-methyl ketone, $C_6H_4<\begin{matrix}N{:}N\\|\\N{:}C\end{matrix}Ac$, is obtained by the action of mineral acids on formazyl methyl ketone; it crystallises in yellow, glistening needles, melts at 121·5—122·5°, has feebly basic properties, and is readily soluble in mineral acids, alcohol, and chloroform, insoluble in water and light petroleum. The *phenylhydrazone*, $C_7H_4N_2{\cdot}CMe{:}N{\cdot}NHPh$, resembles azobenzene in appearance, and crystallises in flat, brick-red, lustrous needles melting at 202° with previous softening; with sulphuric acid, a greenish-brown coloration is produced, changing to deep blue on the addition of potassium dichromate or ferric chloride.

On reduction with stannous chloride in acid solution, phenotriazyl methyl ketone yields a compound which crystallises in prisms, melts at 165°, and is being further investigated.

By the action of ammonium sulphide on formazyl methyl ketone in alcoholic solution, a reduction product is obtained which crystallises in flat, yellow, lustrous needles, melts at 183°, and may be recrystallised from water. The substance is probably represented by the formula $C_6H_4<\begin{matrix}NH{\cdot}NH\\|\\N{=}C{\cdot}CHMe{\cdot}OH\end{matrix}$; on treatment with acetic anhydride, an anhydro-derivative, $C_{11}H_{11}N_3O$, is formed; this crystallises in vitreous, lustrous needles melting at 88—89°, has well marked basic properties, readily dissolves in acids, and is reprecipitated by alkalis; attempts to regenerate the preceding yellow compound were unsuccessful.

Four different substances are formed by the interaction of phenylhydrazine and formazyl methyl ketone.

On allowing the substances to react at low temperatures in glacial acetic acid solution, *formazyl methyl ketone phenylhydrazone*,

$$NPh{:}N{\cdot}C(N{\cdot}NHPh){\cdot}CMe{:}N{\cdot}NHPh,$$

is obtained, and crystallises in black, lustrous needles, with a dark steel blue reflex; it melts at 165°, and is soluble in chloroform, with a red colour.

Phenylazomethylosotriazone, $NPh<\begin{matrix}N{:}CMe\\|\\N{:}C{\cdot}N{:}NPh\end{matrix}$, is formed by boiling formazyl methyl ketone with phenylhydrazine in acetic acid solution, or by heating the preceding compound for a short time at 170—180°; it crystallises in long, slender, golden-yellow, lustrous needles, melts at 122°, and is readily soluble in light petroleum or alcohol; the substance is a feeble base, and dissolves in concentrated sulphuric acid with a dark, orange-red colour.

On heating formazyl methyl ketone with phenylhydrazine alone, nitrogen is evolved, and two compounds are formed; the one (m. p. 183°) is identical with the reduction product obtained by the action of ammonium sulphide (see above); the second is colourless and crystalline, and will be further investigated.

The purification of formazyl methyl ketone has hitherto been a matter of difficulty owing to the simultaneous formation of phenylazoformazyl; this can be avoided by the use of sodium carbonate solution instead of soda; the best method of preparation consists in treating pyruvic aldehyde hydrazone with concentrated aqueous diazobenzene at 0°; the mixture is then gradually added to a well cooled solution of sodium carbonate.

Sodioformazyl methyl ketone, NPh:N·CAc:N·NNaPh, crystallises with 1 mol. of alcohol in red prisms, and is decomposed by water. The *potassium* derivative resembles the sodium salt. The *silver* and *copper* derivatives form dark-coloured powders.

Diparatolyl formazyl methyl ketone, $C_6H_4Me·N:N·CAc:N·NH·C_6H_4Me$, is prepared from potassium acetoacetate, paradiazotoluene, and sodium acetate; it crystallises in slender, lustrous, brick-red needles melting at 153—154°; it is readily soluble in benzene, ether, and chloroform, and gives a blue coloration with concentrated sulphuric acid.

α-Paranitrophenyl-h-phenylformazyl methyl ketone,

$$NO_2·C_6H_4·N:N·CAc:N·NHPh,$$

is obtained from paranitrodiazotoluene and pyruvic aldehyde hydrazone, and crystallises in lustrous, dark, ruby-red needles which exhibit a steel-blue, metallic reflex; it melts at 180°, and is sparingly soluble in alcohol or ether. With concentrated sulphuric acid, a violet-red colour is formed.

α-Paratolyl-h-phenylformazyl methyl ketone,

$$C_6H_4Me·N:N·CAc:N·NHPh,$$

is prepared from paradiazotoluene in a similar manner to the preceding compound; it crystallises in lustrous, dark garnet-red plates and melts at 126°. A reddish-violet coloration is produced with concentrated sulphuric acid.

Di-α-naphthylformazyl methyl ketone, $C_{10}H_7N:N·CAc:N·NHC_{10}H_7$, is formed by the action between potassium acetoacetate, α-diazonaphthalene, and sodium acetate; it is very sparingly soluble, is deposited in slender, dark green, lustrous needles, melts at 174·5—175°, and gives a bluish-green colour with concentrated sulphuric acid.

J. B. T.

Behaviour of certain Aromatic Isonitrosoketones towards Acetic Anhydride and Acetic Chloride. By H. G. Söderbaum (*Ber.*, **25**, 3459—3467; compare Abstr., 1891, 1043).—The *acetyl* derivative of paratoluylformoxime (nitrosomethylparatolyl ketone, see Müller and v. Pechmann, Abstr., 1890, 52), prepared by the action of acetic anhydride at the ordinary temperature, crystallises in large, rectangular tables, melts at 67—68°, and is converted into paratoluic acid and hydrogen cyanide by cold aqueous alkali hydroxides, alkali carbonates, or concentrated sulphuric acid. When heated on the water-bath for 2—3 hours with an excess of acetic anhydride, *paratoluyl cyanide*, $C_6H_4Me·CO·CN$, is formed; this crystallises in long, colourless prisms, melts at 52°, and is soluble in the ordinary solvents, water being an exception. It gives paratoluic acid on boiling with alkali, and its vapour has a pleasant odour. Paratolylformoxime is readily soluble in acetic chloride, and, on cooling to 0°, an unstable chloride

separates which decomposes, when treated with water, into the *acetyl* derivative, $C_6H_4Me\cdot C(OH)_2\cdot CH{:}NOAc$; the latter melts at 148°, is readily soluble in alcohol, sparingly so in ether and benzene, and yields Claus and Kroseberg's paratolylhydroxyacetic acid (Abstr., 1887, 949) on treatment with cold sodium hydroxide, cold concentrated sulphuric acid, or boiling dilute hydrochloric acid.

Xyloylformoxime, $C_6H_3Me_2\cdot CO\cdot CH{:}NOH$ [$Me_2 : CO = 1:3:4$], prepared by Claisen's method from the corresponding xylyl methyl ketone, sodium ethoxide, and amyl nitrite, crystallises in long, delicate, white needles, and melts at 94—95°. Its *acetyl* derivative, $C_6H_3Me_2\cdot CO\cdot CH{:}NOAc$, obtained by the action of acetic anhydride in the cold, crystallises in white needles, melts at 53—54°, and, on hydrolysis with alkali, yields the *acid* $C_6H_3Me_2\cdot COOH$, melting at 126°. The *cyanide*, $C_6H_3Me_2\cdot CO\cdot CN$, is formed when the acetyl derivative is digested for 2—3 hours on the water-bath with acetic anhydride; it crystallises from light petroleum in long, white needles, melts at 47°, and is soluble in most organic solvents. The *acetyl* derivative, $C_6H_3Me_2\cdot C(OH)_2\cdot CH{:}NOAc$, obtained from xyloylformoxime and acetic chloride, crystallises from chloroform in small, white needles, melts at 142°, and yields *dimethylmandelic* acid together with xylylformoïn (see this vol., i, 169) on treatment with cold alkali. The dimethylmandelic acid crystallises in thin, six-sided, colourless leaflets, and melts at 103°.

Parabromobenzoylformoxime, $C_6H_4Br\cdot CO\cdot CH{:}NOH$, obtained from acetylbromobenzene (Schweitzer, Abstr., 1891, 684), sodium ethoxide, and amyl nitrite, crystallises in flat, lustrous, yellowish needles, and melts at 164°. The *acetyl* derivative, $C_6H_4Br\cdot CO\cdot CH{:}NOAc$, crystallises from methyl alcohol in stout, four-sided tables, melts at 89°, and yields parabromobenzoic acid (m. p. 251—252°) on hydrolysis with alkali. Parabromobenzoic acid is also the chief product when the oxime is boiled with acetic anhydride. A *chloride*,

$$C_6H_4Br\cdot CCl(OH)\cdot CH\cdot NOAc,$$

is formed when finely powdered parabromobenzoylformoxime is mixed with acetic chloride, and allowed to remain therewith; it commences to sinter at 120°, but only fuses completely at 150°. On treatment with water, it yields the *acetyl* derivative, $C_6H_4Br\cdot C(OH)_2\cdot CH{:}NOAc$, which crystallises in small, white needles, melts at about 153°, and is converted into *parabromomandelic acid* on hydrolysis with alkali. The latter crystallises in delicate, white needles, and melts at 117—118°.

A. R. L.

Preparation and Nitration of Orthochlorobenzaldehyde. By H. Erdmann (*Annalen*, **272**, 148—156).—In chlorinating the chlorotoluenes at a high temperature, the substitution of the hydrogen atoms of the side chain takes place three or four times more quickly when 2 to 3 per cent. of phosphorus pentachloride is added as a chlorine carrier; the reaction must also be carried out in bright daylight, and the gas employed be quite dry and in a fine stream, otherwise most of the chlorine passes through the liquid without being absorbed.

For the preparation of orthochlorobenzaldehyde, dry orthochlorotoluene (750 grams) is chlorinated at 150—180° under the conditions

just mentioned, the process being interrupted as soon as a gain in weight of 380—400 grams has taken place. The crude orthochlorobenzalchloride (1100 grams) is then stirred with a cold mixture of concentrated sulphuric acid (2200 grams) and 10 per cent. anhydrosulphuric acid (2200 grams) in a vessel surrounded by water; after a few minutes, evolution of hydrogen chloride sets in and the temperature of the mixture gradually falls from about 21° to 11·5° in the course of an hour. After stirring for about six hours, the mixture is placed in a separating funnel and kept over night; the acid solution of the chlorobenzaldehyde is then run on to ice, the aldehyde separated, washed, dried, and repeatedly fractionated. The yield of chlorobenzaldehyde, collected within a range of $2\frac{1}{2}°$, is about 170 grams, and further quantities can be obtained from the other fractions.

Nitrochlorobenzaldehyde [Cl : CHO : NO_2 = 1 : 2 : 4], prepared from chlorobenzaldehyde, crystallises in stellar groups of needles or in plates, melts at 80°, and forms an *oxime* melting at 147—148°. On oxidation with potassium permanganate, it is converted into the corresponding chloronitrobenzoic acid, and when its diazo-derivative is decomposed with cuprous chloride, paradichlorobenzaldehyde is formed. F. S. K.

Aluminium Chloride and Nitro-compounds. By F. Stockhausen and L. Gattermann (*Ber.*, **25**, 3521—3525).—The aluminium chloride employed in these experiments was specially prepared by passing hydrogen chloride over aluminium turnings heated in a wide combustion tube, by which means it can readily be obtained quite pure in fairly large quantities. The pure compound is much more active than the commercial article, the reactions proceeding more quickly and giving better yields, whilst some reactions which do not take place when the crude compound is employed can be readily carried out with the pure substance.

Aluminium chloride reacts very violently when mixed with nitrobenzene, carbonisation taking place to a large extent; if, however, the nitrobenzene is diluted with light petroleum, the two compounds unite in molecular proportion, forming a crystalline substance; other nitro-derivatives behave in a similar manner.

All attempts to carry out the Friedel-Crafts ketone synthesis by the action of aluminium chloride on a mixture of a nitro-compound and acetic chloride were without success. On the other hand, the reaction may be carried out if the nitro-derivatives of the phenol ethers be substituted for those of the hydrocarbons. Thus nitranisoïl and acetic chloride when treated with aluminium chloride in carbon bisulphide solution yield *acetonitranisoïl*, $MeO{\cdot}C_6H_3Ac{\cdot}NO_2$, which crystallises from alcohol in long, colourless needles melting at 99·5°. The yield is, however, small, as the nitranisoïl is itself hydrolysed by the action of the aluminium chloride, the liquid containing, in addition to the above compound, orthonitrophenol and nitrohydroxyacetophenone. The acetyl group in these compounds probably occupies the para-position relatively to the methoxyl group. Orthonitrophenetoïl yields a similar ketone, $EtO{\cdot}C_6H_3Ac{\cdot}NO_2$, which crystallises in colourless needles and melts at 66—67°.

H. G. C.

Aromatic Alkyl Ketones. By A. Claus (*J. pr. Chem.* [2], **46**, 474—496; compare Abstr., 1891, 1222; 1892, 985).—*Metaxylyl propyl ketone* [$Me_2 : COPr^{\alpha} = 1 : 3 : 6$] is a colourless, refractive, aromatic, oily liquid; it boils at 251° (uncorr.), and dissolves in the usual solvents except water. By oxidation with potassium permanganate it yields orthoparadimethylbenzoylformic acid (metaxylylglyoxylic acid, Abstr., 1891, 564). By reduction in alkaline solution it yields *metaxylylpropylcarbinol* [$Me_2 : CHPr{\cdot}OH = 1 : 3 : 6$], which is a yellow oil, and boils above 270°. The *oxime* was also prepared. *Metaxylylbutyramide*, $C_6H_3Me_2{\cdot}[CH_2]_3{\cdot}CONH_2$ [$= 1 : 3 : 6$], was prepared from the ketone by Willgerodt's reaction (heating with yellow ammonium sulphide containing sulphur); it crystallises in colourless, flat needles, melts at 123—124°, and dissolves in most solvents. *Metaxylylbutyric acid* crystallises in colourless needles, and melts at 70°; its *potassium*, *sodium*, *barium* (with $4H_2O$), *calcium* (with $4H_2O$), *copper*, *lead*, and *silver* salts were prepared.

Paraxylyl propyl ketone [$Me_2 : COPr^{\alpha} = 1 : 4 : 2$] is a colourless, oily liquid, of characteristic odour and lower sp. gr. than water; it boils at 249°. The *oxime* forms thick, colourless needles, and melts at 47°. *Paraxylylbutyramide* (m. p. 125°) and *paraxylylbutyric acid* (m. p. 70°) are similar in all respects to the metaxylyl derivatives (see above); the same salts were prepared and found to contain the same water of crystallisation.

Tolyl isopropyl ketone [$Me : COPr^{\beta} = 1 : 4$] is a colourless, refractive liquid, of aromatic odour and bitter taste; it boils at 235—236°. The *oxime* crystallises in colourless, hexagonal tables and in flat needles, and melts at 92°. By reduction with sodium amalgam, the ketone yields an oil which crystallises and then melts at 199°; when zinc and alcoholic potassium hydroxide are used, *tolylisopropylcarbinol* is obtained; this is a thick, yellowish-brown oil, which boils above 300°. By oxidation with alkaline potassium permanganate, the ketone yields only paratoluic and terephthalic acids.

Metaxylyl isopropyl ketone [$Me_2 : COPr^{\beta} = 1 : 3 : 6$] is a colourless oil which boils at 244—245°. The *phenylhydrazide* melts at 128—129°, and the *oxime* at 97°. The reduction products (compare above) melt at 110° and boil about 300° respectively, but are not yet identified. Oxidation of the ketone by dilute aqueous potassium permanganate yields metaxylylglyoxylic acid; this is the first isopropyl ketone in which the authors have observed an oxidation of the secondary alkyl group to carboxyl with formation of the corresponding α-ketonic acid. The ketone can, with difficulty, be converted into *metaxylylisobutyramide* [$Me_2 : CH_2{\cdot}CHMe{\cdot}CONH_2 = 1 : 3 : 6$], and the yield is small; this compound crystallises in needles and melts at 120°; the corresponding *acid* forms colourless, nacreous crystals, and melts at 70°.

Paraxylyl isopropyl ketone [$Me_2 : COPr^{\beta} = 1 : 4 : 2$] is a colourless oil having a mushroom-like odour and bitter taste; it boils at 239—240°. The *oxime* crystallises in small tables and prisms, and melts at 76°.

Orthoxylyl isopropyl ketone [$Me_2 : COPr^{\beta} = 1 : 2 : 4$], is a colourless oil of faint turpentine-like odour, and boils at 255—258°. The *oxime* forms large, vitreous prisms, and melts at 68°. Oxidation of the

ketone with aqueous potassium permanganate yields no ketonic acid but plenty of metaparadimethylbenzoic acid (m. p. 163°).

Paraisocymyl isopropyl ketone [Me : Pr^{β} : $COPr^{\beta}$ = 1 : 4 : 2] is a pale yellow, oily liquid of sp. gr. 0·957 at 19°, and boils at 259°. The *phenylhydrazide* is a yellow oil which cannot be crystallised. The *oxime* is a pale yellow oil which, like the oximes of other ketones containing isocymyl, cannot be crystallised. When the ketone is reduced with iodine and phosphorus (compare Abstr., 1892, 985), *orthoisobutylparaisopropyltoluene* [Me : Pr^{β} : CH_2Pr^{β} = 1 : 4 : 2] is obtained; it is a colourless liquid of sp. gr. 0·916 at 17°, and boils at 230°.

Paraisocymyl ethyl ketoxime is a yellow, uncrystallisable oil.

Orthopropylparaisopropyltoluene [Me : Pr^{α} : Pr^{β} = 1 : 2 : 4] is a colourless, refractive liquid of sp. gr. 0·902 at 17°, and boils at 225°.

Isocymyl propyl ketoxime is a viscid oil.

Orthobutylparaisopropyltoluene [Me : Pr^{β} : C_4H_9 = 1 : 4 : 2] is a colourless, refractive liquid, of sp. gr. 0·892 at 17°, and boils at 235°.

Paraisocymyl isobutyl ketone [Me : Pr^{β} : $CO{\cdot}C_4H_9$ = 1 : 4 : 2] is a nearly colourless, refractive oil of sp. gr. 0·944 at 19°, and boils at 270—272°. The *phenylhydrazide* is a dark red oil; the *oxime* is a pale yellow, viscid oil. By reduction with phosphorus and iodine, the ketone yields *orthoisoamylparaisopropyltoluene* [Me : Pr^{β} : C_5H_{11} = 1 : 4 : 2], a colourless, mobile oil, which boils at 245°, and has sp. gr. 0·89 at 17°.

Phenyl isobutyl ketone has been described before (*Beilstein* [2], 3, 84); its *oxime* melts at 74°. Isoamylbenzene is also known (*loc. cit.*, p. 26).

Metacymyl methyl ketone [Me : Pr^{α} : COMe = 1 : 3 : 4] is a colourless liquid, specifically lighter than water; it boils at 248—252°. The *oxime* is a yellow, viscid oil. *Metacymylglyoxylic acid* [Me : Pr^{α} : $CO{\cdot}COOH$ = 1 : 3 : 4] is described, together with its *barium* (with H_2O), *calcium* (with $2H_2O$), and *copper* salts. *Metacymylcarboxylic acid* [Me : Pr^{α} : COOH = 1 : 3 : 4] melts at 75—76°; its *barium* (with $1\frac{1}{2}H_2O$) and *calcium* (with $2H_2O$) salts were prepared. These two acids are the products of the partial oxidation of the ketone with potassium permanganate; ultimately trimellitic acid is produced. A. G. B.

Aromatic Ketones. By F. Stockhausen and L. Gattermann (*Ber.*, **25**, 3535—3538).—No ketones have hitherto been prepared from unsaturated acids by Friedel and Craft's method; the authors find, however, that the synthesis can be accomplished without difficulty.

By the action of cinnamic chloride and ethoxybenzene dissolved in carbon bisulphide on aluminium chloride at ordinary temperatures, a ketone is obtained which has the formula $CHPh{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OEt$; it forms colourless crystals, and melts at 74—75°. On treatment with bromine at the ordinary temperature, an additive compound, $C_{17}H_{16}Br_2O_2$, is obtained which forms colourless crystals, and melts at 150°.

By the action of hydroxylamine on the ketone in alkaline solution,

a compound is obtained which crystallises in small plates melting at 107—108°; it does not appear to be an oxime, since it is not hydrolysed by heating with hydrochloric acid in a sealed tube; it is insoluble in alkali, and yields no acetate on treatment with acetic anhydride, the authors suggest that it is probably represented by the formula

$$CHPh<\begin{matrix}O-N\\ \|\\ CH_2\cdot C\cdot C_6H_4\cdot OEt\end{matrix}$$

A corresponding *methoxy-derivative*, $CHPh{:}CH\cdot CO\cdot C_6H_4\cdot OMe$, is prepared from cinnamic chloride and methoxybenzene; it crystallises in colourless needles melting at 106—107°. The *dibromo-compound*, $C_{16}H_{14}O_2Br_2$, forms needles which melt at 158—159°. With hydroxylamine, a substance is obtained which is analogous to the ethoxy-derivative, and crystallises in pearly, lustrous plates melting at 122—123°.

Cinnamic chloride and α-ethoxynaphthalene also yield a ketone which crystallises from alcohol in needles melting at 85—86°.

Phenylpropiolic chloride, $CPh{:}C\cdot COCl$, is prepared from phenylpropiolic acid and phosphoric chloride; it is a colourless liquid which boils at 130—133° under a pressure of 25—30 mm., and solidifies on cooling. The *amide*, $CPh{:}C\cdot CO\cdot NH_2$, crystallises from water in colourless needles melting at 99—100°. The *anilide* is deposited in needles which melt at 125—126°. On treating phenylpropiolic chloride with methoxybenzene and aluminium chloride, a ketone, $CPh{:}C\cdot CO\cdot C_6H_4\cdot OMe$, is obtained which crystallises in colourless needles melting at 100°. By the action of bromine at the ordinary temperature, a dibromo-additive compound, $C_{16}H_{12}O_2Br_2$, is formed; it forms colourless crystals, and melts at 138—140°.

The authors failed to obtain ketones by the action of aromatic hydrocarbons on cinnamic chloride in presence of aluminium chloride.

J. B. T.

Azoxybenzoic acids. By N. N. Uspensky (*J. Russ. Chem. Soc.*, **23**, 89—92).—10 grams of orthonitrobenzoic acid, 10 grams of potash in small pieces, and 10 grams of alcohol were heated together, and the alcohol distilled off after the completion of the reaction. The residue was dissolved in water, and precipitated with hydrochloric acid. The impure orthazoxybenzoic acid thus obtained was purified by conversion into the soluble barium salt, from solutions of which the acid may be precipitated in the crystalline form.

The pure acid, $ON_2(C_6H_4\cdot COOH)_2$, forms large, prismatic, transparent, brownish-yellow crystals belonging to the triclinic system. It is very soluble in boiling alcohol, but only slightly soluble in ether or in boiling water. At 200°, it begins to decompose, and at 237°, melts with formation of a black mass. The methyl salt, prepared by passing hydrogen chloride into a solution of the acid in methyl alcohol, is a solid which crystallises from alcohol in long, golden-yellow prisms, and melts at 115·5°.

40 grams of metanitrobenzoic acid, 40 grams of potash, and 300 grams of alcohol were heated for 12 hours, using a reflux condenser. The crude metazoxybenzoic acid obtained after distilling off the alcohol and precipitating with hydrochloric acid, was purified by dissolving

it in ammonia, and precipitating the acid impurities by means of calcium chloride. The filtrate, on treatment with hydrochloric acid, gave about half the theoretical quantity of metazoxybenzoic acid in the form of a slightly yellow, amorphous mass, insoluble in water, alcohol, and ether. From boiling acetic acid, it separates in the form of yellow, microscopic prisms. Large crystals may be obtained by dissolving the acid in acetic acid at 200° in a sealed tube, and allowing it to cool very slowly. It melts at 320° with decomposition, the upper part of the tube becoming covered with a white deposit.

By employing sodium methoxide and methyl alcohol instead of potash and ethyl alcohol in the preparation of the azoxybenzoic acids, a better yield of pure substance is obtained. Thus 40 grams of metanitrobenzoic acid, boiled for 20 hours in a solution of 30 grams of sodium in 250 grams of methyl alcohol, gave 25 grams of almost colourless metazoxybenzoic acid. 10 grams of the orthonitro-acid, similarly treated, gave 8 grams of the pure azoxy-acid. Paranitrobenzoic acid, under the same circumstances, gave no azoxy-acid, but a good yield of pure parazobenzoic acid. J. W.

Action of Phosphorus Pentachloride on Azo- and Azoxybenzoic acids. By N. N. Uspensky (*J. Russ. Chem. Soc.*, **23**, 92—94).—Parazobenzoic acid was heated in a flask with twice its weight of phosphorus pentachloride until the whole fused to a homogeneous, coloured liquid, which solidified to a crystalline mass on cooling; this was washed with ether in order to remove phosphorus oxychloride, and recrystallised from benzene or light petroleum. The red needles thus obtained were crystals of the acid chloride, $N_2(C_6H_4{\cdot}COCl)_2$, easily soluble in benzene and light petroleum, soluble with difficulty in ether, and melting at 144·5—145°. With ethyl alcohol, the acid chloride at once gives the corresponding ethyl salt, which melts at 114·5°.

Metazobenzoic acid, when treated in like manner, gives an acid chloride melting at 97°.

Metazoxybenzoic acid gives an acid chloride which crystallises in almost colourless needles, easily soluble in benzene, and melting at 120—121·5°. The ethyl salt obtained from the acid chloride melts at 76—78°.

Orthazoxybenzoic acid reacts violently in the cold with phosphorus pentachloride, with formation of a tarry mass. When the action takes place in presence of a large quantity of benzene, a crystalline mass of yellow needles is obtained. These needles melt at 210°, but only contain 13·10 per cent. of chlorine instead of the 21·98 per cent. demanded by the formula $N_2O(C_6H_4{\cdot}COCl)_2$. The author considers them to be the half acid chloride $COCl{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}COOH$.

Orthazobenzoic acid yields no crystalline substance with phosphorus pentachloride, either by itself or in presence of benzene. J. W.

Salicylide. By R. Anschütz (*Ber.*, **25**, 3506—3512).—Up to the present, only one member of the lactide group has been definitely prepared, namely, lactide itself; glycolide, from its physical properties, must have a higher molecular weight than is indicated by the

formula $CH_2<^{CO\cdot O}_{O\cdot CO}>CH_2$. In the aromatic group, the only known substance which might belong to this group is the so-called salicylide obtained by the action of phosphorus oxychloride on salicylic acid; this substance, however, as hitherto prepared, is not a homogeneous compound. The author has now succeeded in obtaining it in a pure condition, by dissolving salicylic acid in toluene or xylene, and gradually adding an equal weight of phosphorus oxychloride to the warmed solution. When crystallised from chloroform, it forms transparent, tetragonal crystals ($a : c = 1 : 1{\cdot}4530$), which contain chloroform and have the formula $C_{28}H_{16}O_8,2CHCl_3$. On heating, chloroform is evolved and salicylide remains as a white substance, which melts at 261—262°, is very slightly soluble in the usual solvents, and is gradually converted by boiling soda into salicylic acid. The residue left after extraction with chloroform is scarcely soluble in the ordinary solvents, but separates from phenol and nitrobenzene in microscopic needles which melt at 322—325° without evolution of gas. It has the same composition as salicylide, and, like the latter, is converted into salicylic acid by long continued boiling with alkalis; it may, therefore, be termed *polysalicylide*, $(C_7H_4O_2)_n$.

Orthohomosalicylic acid, when treated with phosphorus oxychloride, also yields a similar *orthohomosalicylide*, $C_{28}H_{12}Me_4O_8$, which separates from chloroform in tetragonal crystals, likewise containing chloroform, which is evolved at 100°; the residual orthohomosalicylide is even less soluble than salicylide, and melts at 293—295°. Metahomosalicylic acid only yields a compound corresponding with polysalicylide, $(C_7H_3MeO_2)_n$, which is insoluble in chloroform, and after crystallisation from phenol melts at 292—294°. *Parahomosalicylide*, obtained from parahomosalicylic acid, melts at 295—297°, and although soluble in boiling chloroform, does not yield crystals containing that substance.

The determination of the molecular weight of salicylide and its homologues in phenol solution leads to the supposition that they contain the group $C_6H_4<^{CO}_{O}$ four times; the constitution of salicylide is possibly represented by the formula

$$C_6H_4<^{CO\cdot O\cdot C_6H_4\cdot CO\cdot O}_{O\cdot CO\cdot C_6H_4\cdot O\cdot CO}>C_6H_4.$$

The molecular weight of the poly-derivatives could not be ascertained, but lactide gave numbers in phenol solution corresponding with the formula $C_6H_8O_4$, whilst glycolide appears to be $(C_2H_2O_2)_6$. The author proposes, therefore, that lactide should be termed *dilactide*, salicylide *tetrasalicylide*, and so on. H. G. C.

New Phenylamidolactic acid from Glycocine and Benzaldehyde. By E. Erlenmeyer, Jun. (*Ber.*, **25**, 3445—3447).—Benzaldehyde and glycocine, in dilute alcoholic solution, and in presence of sodium hydroxide, form condensation products; from these, boiling alcohol extracts a compound which is under investigation, whilst the residue consists of a sodium salt sparingly soluble in water. On treatment with acetic acid, the latter decomposes, yielding benz-

aldehyde, and if the product is passed through a wet filter, the last-named compound is retained by it; the filtrate, when concentrated, yields phenylamidolactic acid (phenylserine),

$$OH{\cdot}CHPh{\cdot}CH(NH_2){\cdot}COOH.$$

It crystallises in lustrous leaflets with 1 mol. H_2O, melts with decomposition at 192—193°, or after drying at 100° at 195—196°; it is sparingly soluble in water, and almost insoluble in alcohol. When the acid is treated with potassium nitrite and hydrochloric acid, ether extracts phenylglyceric acid, and on warming the latter with concentrated sulphuric acid, it is converted into a compound giving, with ferric chloride, the green colour reaction characteristic of phenylpyruvic acid.

By condensing benzaldehyde with hippuric acid, a *lactimide*, probably $CPhO{\cdot}N<\begin{matrix}C(CHPh){\cdot}CO\\CO{\cdot}C(CHPh)\end{matrix}>N{\cdot}CPhO$, is obtained, and an acetylbenzoyl derivative of the above described phenylamidolactic acid is perhaps an intermediate product of the reaction. In support of this view, it is found that this phenylamidolactic acid, when heated with acetic anhydride and sodium acetate, yields a lactimide closely resembling that mentioned above. The author hopes to be able to synthesise serine from formaldehyde and glycocine. A. R. L.

Methylation of Opianic acid. By R. Wegscheider (*Monatsh.*, 13, 702—715; compare Abstr., 1892, 1208).—The author has investigated the action of methyl iodide on lead opianate; of methyl alcohol on opianic chloride; and, lastly, of methyl alcohol on (1) opianic acid and (2) its methyl salt, in presence of hydrochloric acid. The results obtained show that in every case the formation of the pseudomethyl salt, $C_6H_2(OMe)_2<\begin{matrix}CH(OMe)\\CO\end{matrix}>O$, which melts at 103°, depends on the attachment of the methyl alcohol to the COH group. When this reaction is prevented, the formation of the true methyl salt, $CHO{\cdot}C_6H_2(OMe)_2{\cdot}COOH$, invariably follows. G. T. M.

Anilide of Gallic acid. By H. Schiff (*Annalen*, **272**, 234—238).—*Gallanilide*, $C_6H_2(OH)_3{\cdot}CO{\cdot}NHPh + H_2O$, can be obtained by heating tannin with anhydrous aniline sulphite (compare *Annalen*, **140**, 126) at 90—120°, and crystallising the solid product from dilute sulphurous acid; it is then treated with dilute ammonium carbonate to free it from gallic acid. It forms large, lustrous, colourless plates, melts at 207°, loses its water at 100°, and gives a red coloration with alkalis; in very dilute solutions, ferric chloride produces a violet, in more concentrated solutions a bluish-green coloration. The *triacetyl* derivative, $C_6H_2(OAc)_3{\cdot}CO{\cdot}NHPh$, crystallises from dilute alcohol in colourless, concentrically-grouped needles, and melts at 101—102°.

Aniline gallate, $NH_2Ph,C_7H_6O_5$, is formed when gallic acid is heated with aniline at 100°; it crystallises from water and from alcohol, melts at 168° with decomposition into its components, and is slowly decomposed by boiling water. F. S. K.

Synthesis of Symmetrical Diphenylsulphoneacetone by means of Symmetrical Dichloracetone. By R. Otto and J.

Tröger (*Ber.*, **25**, 3422—3425; compare Abstr., 1889, 1186).—Symmetrical diphenylsulphoneacetone is obtained by boiling dichloracetone dissolved in benzene for several days in a reflux apparatus with anhydrous sodium benzenesulphinate; the intermediate *compound*, $CH_2Cl{\cdot}CO{\cdot}CH_2SO_2Ph$, is also formed; it gives methylphenylsulphene (m. p. 88—89°) on treatment with alkali. Diphenylsulphoneacetone is also produced, together with other compounds, by oxidising dithiophenylacetone dissolved in benzene with potassium permanganate and sulphuric acid. The dithiophenylacetone is obtained by the action of the sodium derivative of thiophenol on dichloracetone in alcoholic solution. A. R. L.

Nitrosulphonic acids. By H. Limpricht (*Ber.*, **25**, 3477).—The author finds that the compound described by him as nitrosobenzenesulphonic acid (Abstr., 1892, 475) is a nitrobenzenesulphinic acid. The nitrosulphinic acids which have been examined, namely, metanitrosulphinic, ortho- and para-nitrotoluenesulphinic, and nitronaphthalenesulphinic acids, all give a blue colour with phenol and sulphuric acid, similar to that obtained with nitroso-compounds. Metanitrobenzene sulphobromide also gives a blue coloration with phenol and sulphuric acid, but the sulphochloride does not. E. C. R.

Benzenesulphonamides. By O. Hinsberg (*Annalen*, **272**, 229—233; compare Abstr., 1892, 64).—*Benzenesulphoneamidoazobenzene*, $SO_2Ph{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph$, prepared by warming benzenesulphonic chloride with amidoazobenzene in benzene solution, crystallises from dilute alcohol in yellowish needles, and melts at 133°; it forms a yellow, sparingly soluble sodium derivative.

Dibenzenesulphonebenzidine, $SO_2Ph{\cdot}NH{\cdot}C_{12}H_8{\cdot}NH{\cdot}SO_2Ph$, is formed when finely-divided benzidine is shaken with soda and benzenesulphonic chloride; it is a colourless, crystalline substance, melts at 232°, and is only sparingly soluble in all ordinary solvents.

Benzenesulphonebenzidine, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}SO_2Ph$, is also produced under the conditions first mentioned, and can be separated from the preceding compound by solution in hydrochloric acid; it crystallises from dilute alcohol in colourless needles melting at 160—161°.

Dibenzenesulphonedimethylbenzidine, $C_{26}H_{24}N_2S_2O_4$, is obtained when dibenzenesulphonebenzidine is treated with methyl iodide and soda in alcoholic solution; it crystallises in small, colourless needles, and melts at 179—180°.

Dibromodiethyldibenzenesulphoneparaphenylenediamine,

$$C_6H_4[N(SO_2Ph){\cdot}C_2H_4Br]_2,$$

is formed when dibenzenesulphoneparaphenylenediamine is treated with ethylene bromide and alcoholic potash; it crystallises from hot ethylene bromide in colourless prisms, and melts at 192°.

F. S. K.

Thienylindole, α-Naphthylindole, and some Bromo-derivatives of Indoles. By K. Brunck (*Annalen*, **272**, 201—208).—*Thienylindole*, $C_6H_4{<}\overset{CH}{\underset{NH}{>}}C{\cdot}C_4SH_3$, is formed when acetothienone-

hydrazone is heated with anhydrous zinc chloride, it crystallises from alcohol in yellow needles, melts at 162°, sublimes readily, and gives a bluish-violet pine-chip reaction. The *picrate*,

$$C_{12}H_9SN,C_6H_3N_3O_7,$$

crystallises in dark red plates melting at 137°. The *nitroso*-derivative, $C_{12}H_8N_2SO$, separates from boiling glacial acetic acid in microscopic, orange-red plates, darkens at 230°, and melts at 240—241° when quickly heated; it is moderately easily soluble in alkalis, and does not give Liebermann's reaction. The *benzal* derivative,

$$CHPh(C_{12}H_8NS)_2,$$

crystallises from a mixture of alcohol and acetone in yellow plates, melts at 245° with decomposition, and is decomposed by hot concentrated hydrochloric acid.

α-Naphthylindole, $C_6H_4<\begin{matrix}CH\\NH\end{matrix}>C\cdot C_{10}H_7$, prepared by heating the hydrazone of methyl naphthyl ketone with zinc chloride, crystallises from alcohol in pale yellow, concentrically grouped needles, and melts at 196°. The *picrate*, $C_{24}H_{16}N_4O_7$, forms purple-red scales, and melts at 179°. The *nitroso*-derivative, $C_{18}H_{12}N_2O$, crystallises from glacial acetic acid in yellowish-red plates, and melts at 248° with decomposition. The *benzal* derivative, $CHPh(C_{18}H_{12}N)_2$, separates from acetone in reddish plates melting at 246°.

A *bromo*-derivative, which is probably a tetrabromophenylindole dibromide, $C_{14}H_7NBr_6$, is formed when a chloroform solution of phenylindole is gradually added to a large excess of bromine and the mixture then carefully warmed; it crystallises from hot benzene in colourless, well-defined plates melting at 259—260°. It does not form a compound with picric acid, does not show the pine-chip reaction, and is not acted on by boiling hydrochloric acid or boiling nitric acid.

The *bromo*-derivative of the composition $C_{12}H_5NSBr_6$, prepared from thienylindole in like manner, separates from benzene in plates, and melts at 278°; the compound of the composition $C_{18}H_9NBr_6$, obtained from α-naphthylindole, crystallises in yellow plates melting above 300°.

When methylketole (methylindole) is treated with excess of bromine at the ordinary temperature, it yields two products, one of which crystallises from glacial acetic acid in yellowish needles, melts at 195°, and has the composition $C_9H_7NBr_4$; the other product is insoluble in glacial acetic acid, and melts above 300°. F. S. K.

Aromatic Tetraketones. By P. W. Abenius and H. G. Söderbaum (*Ber.*, **25**, 3468—3476).—The authors find that the reaction by which the hydrate of an acetylated aromatic isonitrosoketone when treated with sodium carbonate is converted into a hydroxytriketone is of general application.

Diphenylhydroxytriketone, when treated with hydroxylamine hydrochloride in alcoholic solution, yields the anhydrides of its mono- and di-oxime, a compound $C_{18}H_{16}O_4$, and also a small quantity of the dioxime of the tetraketone, which remains in the mother liquors.

The above three compounds are separated partly by fractional crystallisation from alcohol and partly by mechanical means.

The *anhydride of the monoxime*, $\begin{matrix}\text{CPh·CO}\\ \|\\ \text{N}\text{---}\text{O}\end{matrix}$>CH·CPhO, crystallises in beautiful, yellow, lustrous scales, melts at 175°, and darkens slightly on exposure to light.

The *anhydride of the dioxime*, $\begin{matrix}\text{CPh·CO}\\ \|\\ \text{N}\text{---}\text{O}\end{matrix}$>CH·CPh:NOH, crystallises in thick, pale yellow rhombohedra, sinters at 185°, melts at 191° with decomposition, and turns brownish-yellow on exposure to light.

The *compound* $C_{18}H_{16}O_4$ crystallises in thick, yellow, rhombic prisms. It is also obtained by reducing diphenylhydroxytriketone with stannous chloride and hydrochloric acid. The *acetyl derivative*, $C_{20}H_{18}O_5$, crystallises in short, white aggregates of prisms, and melts at 121—122°.

Diphenyltetraketonedioxime, $C_2O_2(CPh{:}NOH)_2$, is easily obtained by warming the tetraketone (Abstr., 1892, 69) with hydroxylamine hydrochloride in alcoholic solution. It crystallises with 1 mol. of alcohol in colourless prisms, melts at 176° with evolution of gas, and when heated at 190° yields benzonitrile and oxalic acid, showing that the carbonyl groups which have reacted with hydroxylamine are those united to phenyl.

Benzoylformoxime, when treated with phenylhydrazine acetate in alcoholic solution, yields a brownish, resinous product, from which a small quantity of a crystalline substance melting at 262° can be isolated.

Diphenyltetraketone and phenylhydrazine acetate yield two crystalline compounds which may be separated by crystallisation from ether. The one, easily soluble in ether, crystallises in slender, lustrous needles, and melts at 167°; the other, sparingly soluble in ether, crystallises in colourless needles, and melts at 184°.

Diparatoluylhydroxytriketone,

$$C_6H_4Me·CO·CH(OH)·CO·CO·C_6H_4Me,$$

forms yellow, microscopic crystals, turns red at 140°, and melts at 161° to a red liquid. It has feeble acid properties, and dissolves in alkalis with an intense, reddish-yellow coloration.

Diparatoluyltetraketone hydrate, $C_6H_4Me·CO·C(OH)_2·CO·CO·C_6H_4Me$, crystallises in long, sulphur-yellow prisms, melts at 88°, and sometimes crystallises from carbon bisulphide in beautiful, thick prisms containing carbon bisulphide. The *dioxime*, $C_2O_2[C(NOH)·C_6H_4Me]_2$, crystallises in lustrous, colourless leaflets containing 1 mol. of alcohol, and melts at 181° with decomposition.

Dixylylhydroxytriketone, $C_6H_3^{1,3}Me_2^{4}·CO·CH(OH)·CO·CO·C_6H_3^{1,3}Me_2$, crystallises in slender needles, and melts at 155°.

Dixylyltetraketone, $C_4O_4(C_6H_3Me_2)_2$, crystallises in lustrous, scarlet needles, melts at 180°, is indifferent to alkalis and acids, and is sparingly soluble in the ordinary solvents. The *dihydrate* is obtained by adding a large quantity of water to a solution of the tetraketone

in acetic acid; it crystallises in short, four-sided, yellow prisms, and gradually loses water at 100°, being reconverted into the tetraketone.

Diparabromophenylhydroxytriketone,

$$C_6H_4Br\cdot CO\cdot CH(OH)\cdot CO\cdot CO\cdot C_6H_4Br,$$

crystallises in small prisms or rectangular tablets, reddens at 110°, and melts at 180°.

Diparabromophenyltetraketone hydrate,

$$C_6H_4Br\cdot CO\cdot C(OH)_2CO\cdot CO\cdot C_6H_4Br,$$

crystallises in yellow needles, and, at 135°, melts to a yellow liquid with evolution of gas. E. C. R.

Acetyl Derivatives of 2 : 1-Amidonaphthol. By O. Michel and E. Grandmougin (*Ber.*, **25**, 3429—3434).—When 2 : 1-amidonaphthol hydrochloride is dissolved in water with the addition of concentrated hydrochloric acid, and binormal nitrite solution added at 0°, β-naphthaquinone is the sole product as previously shown (Abstr., 1892, 832). Meldola and Morgan (Trans., 1889, 120) stated that they obtained nitroso-β-naphthol by the action of nitrous acid on 2 : 1-amidonaphthol (Meldola has since confirmed the authors' statement that the product is β-naphthaquinone, Proc., 1892, 218).

When 2 : 1-amidonaphthol hydrochloride is warmed for about two minutes with acetic anhydride, the diacetyl derivative (Meldola and Mozgan, *loc. cit.*) is exclusively formed, whilst by continuing the heating for 3½—4 hours ethenylamidonaphthol (Böttcher, Abstr., 1883, 1113) is also one of the products, and when the mixture is heated in a sealed tube at 130—140° for 1½ hours, a certain quantity of acetamido-β-naphthol is also produced. To separate these three compounds, the mixture is crystallised from alcohol, when the diacetyl derivative is obtained; the alcoholic mother liquor is then poured into water, when ethenylamidonaphthol separates as an oil, whilst acetamido-β-naphthol remains in solution. A mixture of acetamido-β-naphthol and ethenylamidonaphthol is formed by heating 2 : 1-amidonaphthol hydrochloride with glacial acetic acid and anhydrous sodium acetate for some hours. The relative amount of these compounds varies according to the duration of heating; by half an hour's heating, for example, the product is almost exclusively acetamido-β-naphthol, but after 3—4 hours' heating, ethenylamidonaphthol preponderates. A. R. L.

Methylnaphthalenes. By G. Wendt (*J. pr. Chem.* [2], **46**, 317—327).—To separate the α- and β-methylnaphthalenes from each other, the mixture obtained from creosote oil (Schulze, Abstr., 1884, 1183) is cooled until it solidifies, the temperature is then very gradually raised, and the α-methylnaphthalene melted out; this fractional fusion is repeated until the physical constants of the more fusible portion no longer vary (compare Wichelhaus, Abstr., 1892, 492). The proportion of α- to β-methylnaphthalene obtained from the oil by this process was 5 : 2; Schulze (*loc. cit.*) gives the proportion as 2 : 3.

α-Methylnaphthalene is a pale-yellow, mobile oil, stable in air and light; it melts at −22°, and boils at 240—243° (759 mm., mercury column in vapour); its sp. gr. is 1·0005 at 19°. It dissolves in alcohol and ether, but only very slightly in water; it is volatile with steam, a good solvent, a bad conductor of heat, strongly refractive, and non-fluorescent (compare Wichelhaus, *loc. cit.*). It burns with a luminous flame, has a naphthalene-like odour, and a burning, soapy taste.

β-Methylnaphthalene crystallises in transparent laminæ, melts at 32·5°, boils at 241—242° (mercury column in vapour; 759 mm.), and dissolves in most of the usual solvents.

Each methylnaphthalene yields two monosulphonic acids, which can be separated by means of their barium salts, one of which is about six times as soluble as the other. The barium α-methylnaphthalene-sulphonates are about twice as soluble as the β-methylnaphthalene-sulphonates. The lead, potassium, and sodium salts were also isolated. In conclusion, the author criticises Wichelhaus (*loc. cit.*).

A. G. B.

Condensation of Formaldehyde with Naphthols. By J. Abel (*Ber.*, **25**, 3477—3484).—*Di-β-naphtholmethane*,

$$CH_2(C_{10}H_6{\cdot}OH)_2,$$

is obtained by the action of methylene dimethyl ether and fuming hydrochloric acid on β-naphthol. Formaldehyde may be used instead of methylene dimethyl ether. It is easily soluble in dilute alkalis, and is precipitated unchanged by acids. It crystallises in long, silky needles, is not volatile with steam, reddens and sinters at 180°, and melts at 188—189°. It does not give the characteristic colour reactions of β-naphthol. The *picrate* melts at 178—179°. The *acetyl derivative*, $CH_2(C_{10}H_6{\cdot}OAc)_2$, crystallises in slender, lustrous needles, and melts at 212—213°. The *benzoyl derivative*, $CH_2(C_{10}H_6{\cdot}OBz)_2$, crystallises in slender needles, and melts at 158—159°. The *phenylsulphonate*, $CH_2(C_{10}H_6O{\cdot}SO_2Ph)_2$, is obtained by shaking phenyl sulphochloride with a solution of the dinaphtholmethane in aqueous soda. It crystallises in beautiful, colourless, strongly-refractive prisms, and melts at 175°. The *dinitroso-compound*, $CH_2(C_{10}H_5{\cdot}NOH)_2$, is obtained by adding sodium nitrite to a boiling alcoholic solution of the dinaphtholmethane and zinc chloride. It crystallises in brown, lustrous leaflets, is precipitated from its salts by acids in small, yellow needles, containing water of crystallisation, melts at 106° with decomposition, dissolves in alkalis with a green coloration, and closely resembles nitrosonaphthol.

Dibenzeneazodi-β-naphtholmethane, $CH_2[C_{10}H_5(OH){\cdot}N_2Ph]_2$, is obtained by diazotising a mixture of dinaphtholmethane and aniline hydrochloride, and then adding alkali. It crystallises in beautiful needles, having a green lustre, melts at 127—128°, and is soluble in most organic solvents, but insoluble in alkalis. With concentrated sulphuric acid, it yields a magenta solution, and is precipitated unchanged by the addition of water. With concentrated hydrochloric acid, it yields a beautiful red solution.

Diketodinaphthylmethane, $CH_2<\begin{matrix}C_{10}H_6O\\C_{10}H_6O\end{matrix}$, is obtained by treating

β-dinaphtholmethane, dissolved in alkali, with chlorine or bromine water, or with iodine dissolved in potassium iodide. It crystallises in lustrous, sulphur-yellow leaflets, and melts at 168—169°. When reduced with zinc-dust and acetic acid, it is converted into di-β-naphtholmethane. When treated with excess of hydroxlamine hydrochloride, it yields the compound $C_{10}H_6<\begin{matrix}N\cdot O\\ |\\ CH\end{matrix}>C_{10}H_6$. This is insoluble in potassium hydroxide and hydrochloric acid, sparingly soluble in most organic solvents, gives a beautiful red solution with concentrated sulphuric acid, and melts at a high temperature.

Di-α-naphtholmethane is obtained in a similar way to the β-compound as a bright oil, which, after washing with water, forms a hard, brown mass. It dissolves in dilute soda with a beautiful blue coloration, and is precipitated in brown flocks by acids.

Similar condensation products were also obtained from thymol and guaiacol. E. C. R.

Condensation of Chloral Hydrate with Naphthols. By A. Rusanoff (*J. Russ. Chem. Soc.*, **23**, 217—222).—Chloral hydrate (5 grams) and α-naphthol (8·7 grams) are dissolved in acetic acid (15 grams), and to the hot solution is added 1 c.c. of a mixture of equal volumes of acetic and sulphuric acids. When heated on the water-bath, the mixture soon becomes green and turbid, and finally large quantities of crystals separate. These are collected, washed with acetic acid, and dried in a vacuum over sulphuric acid and potash. An analysis of the substance thus obtained corresponded with the formula $CCl_3\cdot CH(C_{10}H_6\cdot OH)_2$. The compound crystallises in slender, transparent needles which become grey on keeping; it does not melt, but gradually blackens at 200°. It is easily soluble in ethyl alcohol, methyl alcohol, ether, and acetone, less soluble in acetic acid, and insoluble in benzene and chloroform. The alcoholic solution turns brown on boiling. On heating at 100° with acetic anhydride and sodium acetate, the salt $CCl_3\cdot CH(C_{10}H_6\cdot OAc)_2$ is obtained in the solid form; on recrystallisation from acetic acid, it forms shining scales, and melts at 176°.

When β-naphthol is heated with chloral hydrate under the above conditions, no change is observed for a long time. Finally, however, the liquid becomes brown, and gives off hydrogen chloride, a brownish oil separating from which crystals may be obtained. These crystals, on purification, melt at 210° with decomposition. They contain no chlorine, and, on analysis, give numbers corresponding with the formula $C_{22}H_{14}O_3$.

If 10 grams of chloral hydrate and 17 grams of β-naphthol are dissolved in 15 grams of acetic acid, and to the solution there is added gradually, with continued shaking, about 20 c.c. of sulphuric acid, viscous lumps separate, which solidify under water. These are dried, mixed with ethyl acetate and then with alcohol, collected, washed with alcohol, and dried. The substance may be crystallised from chloroform (large tables) or from acetic acid (long needles), but only dissolves with difficulty in these and other solvents. The crystals are

greenish, and the acetic acid solution on heating becomes yellow with a green fluorescence. The formula of the compound is

$$CCl_3 \cdot CH < \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > O.$$

It does not give the substance $C_{22}H_{14}O_3$ on being heated with sulphuric and acetic acids. Aqueous or alcoholic alkalis do not dissolve it, nor is it attacked by them even on prolonged heating. It dissolves, however, in hot, strong sulphuric acid with evolution of hydrogen chloride. J. W.

Oxidation of Camphoric acid. By L. Balbiano (*Real. Accad. Linc.*, 1892, i, 278—284).—On oxidising camphoric acid in alkaline solution with permanganate, an *acid* of the composition $C_9H_{16}O_6$ is obtained together with oxalic acid; the new acid is a slightly viscid oil, very soluble in water, alcohol, and ether. The *calcium* salt, $C_9H_{14}O_6Ca$, forms an amorphous, pulverulent mass readily soluble in water. Both the *normal* and *basic barium* salts were prepared; they have the compositions $C_9H_{14}O_6Ba$ and $4C_9H_{14}O_6Ba,BaO$ respectively. The *basic lead* salt, $2C_9H_{14}O_6Pb,PbO$, forms a white powder. The solution of the acid gives no precipitate with copper acetate.

W. J. P.

Action of Hydriodic acid on Piperidine. By E. Spindler (*J. Russ. Chem. Soc.*, **23**, 39—40).—Hofmann (*Ber.*, **14**, 590), by heating pyridine with strong hydriodic acid for a long time at 300°, obtained a hydrocarbon which he judged to be pentane from its boiling point, 35°. Pentamethylene, however, has the same boiling point. The author has therefore again prepared the hydrocarbon obtained by Hofmann. Instead of reducing pyridine, he started from pure piperidine. This substance is not affected by hydriodic acid weaker than sp. gr. 1·96, or at a lower temperature than 300°. On heating with acid of sp. gr. 1·96 at 300° for 10 hours, a hydrocarbon is formed; and this, when washed and dried, distils almost entirely between 33° and 36°, a small quantity remaining which is not volatile at 100°. The sp. gr. of the volatile hydrocarbon is 0·6248 at 17°/17°; that of normal pentane at the same temperature is 0·6263. As the polymethylenes usually differ considerably in their specific gravity from the saturated hydrocarbons containing the same number of carbon atoms, it seems highly probable that the hydrocarbon from pyridine and from piperidine is actually normal pentane. J. W.

Action of Piperidine on Haloïd Salts of Mercury. By R. Varet (*Compt. rend.*, **115**, 880—881).—Piperidine behaves like pyridine and ammonia towards mercuric halides, molecular compounds containing 2 mols. of base to 1 of halide being formed. It decomposes mercurous halides into mercury and mercuric halides, and then unites with the latter.

Piperidine mercurochloride, $2C_5NH_{11},HgCl_2$, made by the direct union of its proximate constituents, crystallises in white, silky tufts of slender needles. It is unstable in the presence of light and air,

and is decomposed by heat, mercury being set free. The *mercurobromide* resembles the mercurochloride, and is prepared in a similar way. It is decomposed by cold water. The *mercurocyanide* crystallises in slender needles, and melts at about 85°. It has less tendency to reduction, and is soluble in cold water without decomposition. The *mercuroiodide*, which also forms white crystals, is more stable than the chloride, but deposits mercury on boiling. JN. W.

New Collidine. By F. AUERBACH (*Ber.*, **25**, 3485—3490).—Aldehydecollidine (b. p. 174 — 178°), prepared from aldehydeammonia and paraldehyde, when oxidised with 2 per cent. potassium permanganate, yields 6-methylnicotinic acid and isocinchomeronic acid and also small quantities of a methylpyridinedicarboxylic acid and an isomeride of the latter. The methylpyridinedicarboxylic acid, $C_5NH_2Me(COOH)_2 + 2H_2O$, crystallises in beautiful white needles, melts at 158°, and loses 1 mol. H_2O at 100°, and the remaining molecule at a higher temperature with partial decomposition. The isomeric acid melts at 178°, but on account of its great solubility has not yet been obtained pure. The formation of these two acids is contrary to the view that collidine is a 2:5-methylethylpyridine, and by fractional crystallisation of the double salt of collidine with mercuric chloride, the author has isolated a second base from aldehydecollidine.

Collidine hydrochloride, when treated with a large excess of mercuric chloride, yields a sparingly soluble double salt of the formula $C_8NH_{11},HCl,6HgCl_2$, a salt of the formula $2(C_8NH_{11},HCl),5HgCl_2$, both derived from the same base, and a salt of a second base of the formula $2(C_8NH_{11},HCl),7HgCl_2$.

The *salt* $C_8NH_{11},HCl,6HgCl_2$ crystallises from hot water in beautiful, rhombic tablets, melts at 168°, and is easily soluble in hydrochloric acid. When allowed to remain some time in a damp state, it is converted into the salt $2(C_8NH_{11}HCl),5HgCl_2$. The latter forms silky needles, and melts at 64°. Pure aldehydecollidine obtained from these salts boils at 173—174° (uncorr.), and has a sp. gr. at 0° = 0·9369; at 23° = 0·9184. The platinochloride, which is crystallographically identical with the salt prepared by Ader and Baeyer (*Annalen*, **155**, 294), crystallises in orange-red prisms, and melts at 182°. The aurochloride crystallises in golden-yellow needles or transparent tablets, and melts at 87°. The picrate melts at 164°, and crystallises in lustrous leaflets.

The *salt* $2(C_8NH_{11},HCl),7HgCl_2$, obtained from the mother liquors of the preceding salt, crystallises in aggregates of beautiful prisms, and melts at 116°. The *new base* obtained from it boils at 177° (uncorr.), and constitutes about 5—10 per cent. of the crude collidine. It is somewhat soluble in water, and has an odour different from that of aldehydecollidine. The *hydrochloride* forms hygroscopic needles. The *platinochloride*, $(C_8NH_{11})_2,H_2PtCl_6$, crystallises in orange-red tablets, and melts at 183° with evolution of gas. The *aurochloride* crystallises from dilute solutions in spangles, and melts at 115°. The *picrate* crystallises in needles, and melts at 123°. E. C. R.

Pipecolinecarboxylic acid. By F. AUERBACH (*Ber.*, **25**, 3490—3493).—The author has prepared the acids α′-methylnicotinic acid and isocinchomeronic acid, and examined the products obtained by reducing them with sodium and absolute amyl alcohol.

2 : 5-Pipecolinecarboxylic acid, $C_7NH_{13}O_3 + \frac{1}{2}H_2O$, is obtained by the reduction of α′-methylnicotinic acid. It melts at 239° when heated in a closed capillary tube, loses its water of crystallisation at 100°, is very hygroscopic, is a very feeble acid, and has basic properties. The *nitroso-compound* is a pale yellow oil. The *hydrochloride* crystallises in large, transparent prisms, and melts at 221—222°. The *platinochloride* is usually obtained as a syrup, but sometimes in beautiful crystals containing water of crystallisation, which it loses at 100—110°; it melts at 199° with decomposition. The *aurochloride* separates in compact crystals, and melts at 185°; its neutral solution decomposes in the cold, and very quickly on boiling, with precipitation of gold and evolution of carbonic anhydride.

By the reduction of isocinchomeronic acid, a small quantity of a *hydrochloride* crystallising in white needles and melting at 235° was obtained. E. C. R.

Action of Nascent Hydrogen on Quinolinic acid. By A. PERLMUTTER (*Monatsh.*, **13**, 840—850).—Following up the analogous work of Wiedel (this vol., i, 114), the author has studied the action of sodium amalgam on an aqueous solution of sodium quinolinate at 90—100°. Reaction occurred much less readily than with most of the analogous acids examined by Wiedel, and only in the presence of much free alkali; the nitrogen of the pyridine ring was eliminated as ammonia and the *lactone* of *αγδ-butenyl-ε-hydroxytricarboxylic acid*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot COOH\\ |\\ CO\text{——}O\cdot CH\cdot COOH\end{matrix}$, obtained. This lactone was purified by conversion into the ethereal salt by means of alcohol and sulphuric acid. The free *lactonic acid* forms a thick syrup, easily soluble in water, alcohol, ethyl acetate, and acetone. The *ethyl salt*, $C_7H_6O_6Et_2$, forms a colourless, thick liquid, almost insoluble in and heavier than water, and having a slight, fruity odour; it cannot be distilled. When an aqueous solution of the lactonic acid is neutralised at 100° with barium carbonate, a *barium salt*, $BaC_7H_6O_6$, is formed. This is easily soluble in water, and the crystals contain water of crystallisation. When a weak solution of this salt is digested with baryta water, *barium hydroxybutenyltricarboxylate*, $Ba_3(C_7H_7O_7)_2$, is formed yielding hairy crystals. Treated with concentrated hydriodic acid, the lactonic acid yields adipic acid, and possibly α-methylglutaric acid. In purifying the adipic acid from ethyl acetate, the author obtained a compound of adipic acid and ethyl acetate, $3C_7H_{10}O_4 + CH_3\cdot COOEt$, crystallising in small, colourless needles.

Amongst the products of the action of sodium amalgam on quinolinic acid, small quantities of a second acid were present; this is possibly the aldehydic acid, $CHO\cdot CH_2\cdot CH_2\cdot CH(COOH)\cdot CO\cdot COOH$.

L. T. T.

Constitution of the so-called Quinoline Ammonium Bases. By W. Roser (*Annalen*, **272**, 221—229).—Numerous observations have led the author to conclude that the peculiar behaviour of the so-called quinoline ammonium bases must be ascribed to their ready conversion into aldehyde or ketone derivatives; quinoline methochloride, for example, may be assumed to readily undergo change into methylamidocinnamaldehyde, $NHMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHO$, in which case its conversion into methylcarbostyril, a reaction first observed by Decker, would be easily explained.

This view of the behaviour of the quinoline ammonium compounds derives its chief support from the fact that they undergo changes very similar to those observed in the cases of hydrastinine and cotarnine.

Attempts to isolate the above-mentioned hypothetical intermediate products have hitherto been unsuccessful. F. S. K.

Action of Benzaldehyde on the Ammoniacal Derivative of Dehydrodiacetyllevulinic acid. By G. Magnanini and M. Scheidt (*Real. Accad. Linc.*, 1892, i, 253—255).—The substance of the composition $C_8H_{11}NO$, which Magnanini obtained (Abstr., 1890, 864) by the action of ammonia on dehydrodiacetyllevulinic acid, yields a condensation product $C_{15}H_{15}NO$ when heated with benzaldehyde and concentrated potash. This compound is readily soluble in alcohol and chloroform, less so in acetic acid, and insoluble in water; it separates from chloroform in small, yellow octahedra which melt at 208·5°, and belong to the orthorhombic system, $a : b : c = 2{\cdot}3333 : 1 : 1{\cdot}9301$. Its molecular weight determined by the cryoscopic method in acetic acid solution is normal.

On distilling the compound $C_8H_{11}NO$ with zinc dust, an oil is obtained, which is, doubtless, a homologue of pyrroline. This and other derivatives of the substance are now being investigated.

W. J. P.

Reduction of 1 : 4 : 5-Phenylmethylethylpyrazole and 1 : 3 : 5-Phenyldimethylpyrazole. By G. Marchetti (*Real. Accad. Linc.*, **7**, ii, 372—377, and *Gazzetta*, **22**, ii, 368—375).—A boiling solution of 1 : 4 : 5-phenylmethylethylpyrazole in absolute alcohol is reduced by slowly adding small pieces of sodium; water is added, the greater part of the alcohol distilled off, and the solution extracted with ether. The ethereal extract is washed with dilute oxalic acid, the ether distilled off, and the residue again reduced; after 10 repetitions of this process, the oxalic acid washings are united and concentrated, rendered alkaline, and repeatedly extracted with ether. The ethereal solution, on evaporation to dryness, yields an oil which rapidly absorbs carbonic anhydride from the air, and boils at 130—160°, in a vacuum, yielding an almost colourless liquid distillate of *methylethylphenyltrimethylenediamine*, $NHPh{\cdot}CHEt{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$. The yield is not increased by using amyl alcohol in place of ethyl alcohol. The base has a nauseating odour, is soluble in alcohol and ether, but only very sparingly so in water; it gives the reactions of a primary amine. The *oxalate* separates from anhydrous alcoholic ether in

small crystals, but is rapidly turned brown by atmospheric moisture. Crystalline salts could not be obtained with sulphuric, picric, uric, or succinic acids; the solution in hydrochloric acid reduces platinic or auric chlorides in the cold. The *benzoyl* derivative is a viscid oil, which, on distillation in a vacuum, yields an oil and a crystalline substance. On suspending the base in water and shaking with carbon bisulphide, evaporating off the latter on the water-bath, and adding alcohol until a clear solution is obtained, *methylethylphenyltrimethylenediamine methylethyltrimethyleneanilthiocarbamate*,

$$NHPh\cdot C_3H_4MeEt\cdot NH\cdot CSSH,NH_2\cdot C_3H_4MeEt\cdot NHPh,$$

is formed, and separates, on cooling, in small needles. It decomposes at 167—170°.

Ether extracts 1 : 3 : 5-phenyldimethylpyrazole from aqueous solutions of its sulphate and oxalate. This pyrazole can be reduced in the same way as the preceding one; on distilling the ethereal extract of the alkaline solution, unaltered dimethylphenylpyrazole is obtained mixed with crystals of 3 : 5-*dimethylpyrazole*. The latter is extracted with hot water, and, on cooling, separates in beautiful laminæ; the yield corresponds with 10 per cent. of the pyrazole employed. Benzene is also found in the alcohol used in the reduction. The reaction is, therefore, represented by the equation $C_3N_2HMe_2\cdot C_6H_5 + H_2 = C_3N_2H_3Me_2 + C_6H_6$.

3 : 5-Dimethylpyrazole is soluble in hot water, alcohol, or ether, melts at 106—107°, and boils at 218° under 758·5 mm. pressure. The *silver* compound, $C_5H_7N_2Ag$, forms a curdy, white precipitate which is not affected by light. The *hydrochloride* is obtained in beautiful, white needles, and is very soluble in water; the *picrate* forms yellow needles. The *platinochloride* crystallises in reddish laminæ or flattened prisms containing 2 mols. of water of crystallisation. It decomposes at 200°, but if kept for some hours at 180—200°, it loses 4 mols. of hydrogen chloride, yielding a red *platinum* compound, insoluble in water. Dimethylpyrazole is oxidised by potassium permanganate, yielding a white, crystalline compound, probably the anhydride of the corresponding dicarboxylic acid. The author is continuing the investigation. W. J. P.

Reduction of 1 : 3 : 5-Phenyldimethylpyrazole. By G. Marchetti (*Real. Accad. Linc.*, 1892, i, 86—92, and *Gazzetta*, **22**, ii, 351—359).—The reduction of 1 : 3 : 5-phenyldimethylpyrazole yields 1 : 3 : 5-*tetrahydrophenyldimethylpyrazole*, in addition to benzene and dimethylpyrazole (compare preceding abstract). The new base is an oil of penetrating, nauseous odour, and boils at 259—260·5° under 758·5 mm. pressure; its sp. gr. at $0°/0° = 1·018$. It does not give the pyrazoline reaction with potassium dichromate and sulphuric acid, and yields well crystallised salts. The *platinochloride*, $(C_{11}H_{16}N_2)_2,H_2PtCl_6$, forms a crystalline precipitate, sparingly soluble in cold water; it melts at 177° with decomposition, but loses hydrogen chloride at 140°, yielding a substance insoluble in water. The action of nitrous acid on the base yields the *nitrate*, $C_{11}H_{16}N_2,HNO_3$, which forms thin prisms and melts at 113°; no nitroso-derivative could be prepared. The base is oxid-

ised by permanganate solution in the cold, being converted quantitatively into dimethylpyrazole and adipic acid. W. J. P.

Constitution of Acetyl-1-phenylpyrazole. By O. Severini (*Real. Accad. Linc.*, **7**, ii, 377—382).—1-*Phenylbromacetylpyrazole* is formed, with evolution of heat, on adding a solution of bromine in glacial acetic acid to 1-phenylacetylpyrazole dissolved in glacial acetic acid. The mixture is allowed to remain 24 hours at the ordinary temperature, or heated on the water-bath for a few minutes. On adding water, the bromo-derivative separates, and is crystallised first from boiling 30 per cent. alcohol, and then from 95 per cent. alcohol; 85 per cent. of the theoretical yield is obtained. It crystallises in white, silky needles, melts at 131—132°, is soluble in ether or hot dilute alcohol, and very sparingly soluble in cold water. On suspending it in water rendered alkaline by aqueous soda, slowly adding potassium permanganate solution, and heating the liquid at 60—70° on the water-bath, oxidation occurs. The solution is concentrated, acidified with sulphuric acid, and extracted with ether; on evaporation, the ethereal solution deposits a ketonic *acid*, $C_3N_2H_2Ph{\cdot}CO{\cdot}COOH$, which separates from dilute alcohol in lustrous needles; it melts at 168° with decomposition, and is soluble in ether. This acid, when dissolved in very dilute caustic potash and oxidised with potassium permanganate solution, yields 1 : 4-phenylpyrazolecarboxylic acid. Phenylacetylpyrazole is therefore a 1 : 4-derivative.

1 : 4-Phenylbromopyrazole does not react with acetic chloride at 280° in a closed tube; the tube exploded at 300—310°. No action occurs with acetic anhydride and sodium acetate at 150—170°.

W. J. P.

Pyrazole Derivatives. By G. Marchetti (*Real. Acad. Linc.*, 1892, i, 356—362, and *Gazzetta*, **22**, ii, 359—367; compare preceding abstract).—3 : 5-*Pyrazoledicarboxylic acid*, $C_3N_2H_2(COOH)_2,H_2O$, is obtained by oxidising the corresponding dimethylpyrazole with potassium permanganate, and crystallises from water in beautiful needles which lose their water of crystallisation at 120°. The anhydrous acid melts at 180° with evolution of carbonic anhydride, and, on distilling it at 280°, pyrazole is obtained. It is soluble in hot water, but only sparingly so in alcohol or ether. The *barium* salt, $C_3N_2H_2(COO)_2Ba,H_2O$, forms a white, crystalline powder.

3 : 5-*Methylpyrazolecarboxylic acid*, $C_3N_2H_2Me{\cdot}COOH$, remains in the mother liquors obtained in the preparation of the preceding acid; it forms small, yellowish crystals, and melts at 235—236° with loss of carbonic anhydride. It is very soluble in hot water, sparingly so in alcohol or ether. The *calcium* salt crystallises in transparent needles or prisms containing 3 mols. H_2O, which are lost at 120°. On distilling the acid, *methylpyrazole*, $C_3N_2H_3Me$, is obtained as a heavy, colourless liquid boiling at 200° under 747·5 mm. pressure; it does not solidify at −16°, and is very soluble in all the solvents. The *picrate* forms small needles melting at 142°, and is very soluble in water. The *platinochloride*, $(C_3N_2H_3Me)_2,H_2PtCl_6,2H_2O$, loses its water of crystallisation in a vacuum, and melts with decomposition at

181°. It is very soluble in water, and loses 4 mols. of hydrogen chloride at 235°, leaving a substance of the composition

$$(C_3N_2H_2Me)_2PtCl_2;$$

this compound gives only traces of platinum tetrachloride when dissolved in dilute aqua regia. W. J. P.

Pyrazolone. By R. v. Rottenburg (*Ber.*, **25**, 3441—3444).—Since v. Pechmann has shown (Abstr., 1892, 816) that the so-called ethyl formylacetate is ethyl β-hydroxyacrylate, it seemed likely that this compound would yield pyrazolone or isopyrazolone on treatment with hydrazine hydrate. Experiment proved, however, that the product of this action is *trimesic trihydrazide*, $C_9H_{12}N_6O_3$, a compound crystallising from absolute alcohol in large leaves and melting at 100° with decomposition.

The discovery of Wislicenus (*Ber.*, **19**, 3225; **20**, 3392), that ethyl oxalacetate yields ethyl phenylpyrazolone-3-carboxylate on treatment with phenylhydrazine, suggested that ethyl pyrazolone-3-carboxylate might be obtained by employing hydrazine hydrate instead of phenylhydrazine. As a matter of fact, this is the case, and the two compounds react energetically, but hydrazine acetate and ethyl oxalacetate only react when heated together, with, however, the formation of ethyl pyrazolone-3-carboxylate and the hydrazide of pyrazolone-3-carboxylic acid.

Ethyl pyrazolone-3-carboxylate, $COOEt\cdot C\begin{cases}N-NH\\ CH_2\cdot CO\end{cases}$, crystallises in colourless needles, melts at 179°, forms a blood-red *isonitroso*-derivative and a red *azo*-compound. *Pyrazolone-3-carboxylic hydrazide*, $NH_2\cdot NH\cdot CO\cdot C\begin{cases}N-NH\\ CH_2\cdot CO\end{cases}$, forms colourless, flat needles, melts at 238°, and is readily soluble in water. *Pyrazolone-3-carboxylic acid* is obtained on hydrolysing the ethyl derivative with alkalis or concentrated hydrochloric acid; it decomposes above 250°, yields a yellowish-red *isonitroso*-derivative, and a red azo-compound. When the basic calcium salt, $NH\begin{cases}N=C\cdot COO\\ CO\cdot CH\cdot Ca\end{cases}$, is heated by itself, or when the acid is heated with soda lime, *pyrazolone*, $CH\begin{cases}N-NH\\ CH_2\cdot CO\end{cases}$, distils over. It is a mobile oil, boils at 77°, has an intense odour of mice, and becomes yellow on exposure to the air; it is readily miscible with water, alcohol, and ether, gives a yellowish-red *isonitroso*-derivative and a blood-red *azo*-compound. Acid oxidising agents, platinic chloride, for example, give rise to a red coloration. A. R. L.

Papaverinic acid. By G. Goldschmiedt and F. Schranzhofer (*Monatsh.*, **13**, 697—701).—*Papaverinic anhydride*, $C_{16}H_{11}NO_3$, crystallises in small needles, melts at 169—170°, and may be sublimed unchanged; the *methyl* salt, $C_{17}H_{15}NO_7$, a yellow, crystalline powder, which dissolves in boiling water without decomposition, melts at 153°; and the *ethyl* salt, $C_{18}H_{17}NO_7$, crystallises in small, white

needles, and melts at 187—188°. The *silver* and *ammonium* salts of *papaverinamic acid*, $C_6H_3(OMe)_2{\cdot}CO{\cdot}C_5NH_3(CONH_2){\cdot}COOH$, are both well characterised. *Anilpapaverinic anilide*, $C_{28}H_{25}N_3O_6$, is an amorphous powder, which commences to sinter at 107° and melts at 119°.

G. T. M.

Laudanine. By G. GOLDSCHMIEDT (*Monatsh.*, **13**, 691—696).—Pure laudanine, $C_{20}H_{25}NO_4$, contrary to Hesse's statement, is optically inactive in alcoholic, as well as in acid, solutions. It crystallises from a mixture of chloroform and alcohol in well-characterised, rhombic prisms [$a : b : c = 0{\cdot}7846 : 1 : 0{\cdot}6124$], and contains three methoxyl groups, having the constitution $C_{17}H_{15}N(OMe)_3OH$. On oxidation with potassium permanganate, in alkaline solution, it is converted into metahemipinic acid, $C_6H_2(MeO)_2(COOH)_2$ [1 : 2 : 4 : 5]. Laudanine is isomeric with tetrahydropapaverine, but is certainly not identical with it.

G. T. M.

Meconinmethyl Phenyl Ketone. By F. v. HEMMELMAYR (*Monatsh.*, **13**, 663—675).—The preparation of this compound from opianic acid and acetophenone has been previously described by Goldschmiedt (compare Abstr., 1892, 179). It has the constitution $\begin{matrix} CO{\cdot}C_6H_3(OMe)_2 \\ | \\ O{-}CH{\cdot}CH_2{\cdot}CPhO' \end{matrix}$, and, when boiled with dilute potash, is resolved into its generators. On heating with phenylhydrazine in sealed tubes at 150—160°, it is converted into the *hydrazone*, $C_{24}H_{22}O_4N_2$, which crystallises from alcohol in needles and melts at 143—144°, or into the *dihydrazone*, $C_{30}H_{28}O_3N_4$, which crystallises from alcohol in yellow masses, sinters at 176°, and is completely molten at 187°. Two oximes, of the formula $C_{18}H_{17}O_5N$, are obtained on heating the ketone with free hydroxylamine in sealed tubes at 150°. Each of these stereoisomerides is almost insoluble in water, and crystallises from alcohol in white needles. They melt at 146° and 198° respectively.

G. T. M.

Cinchona Alkaloïds, particularly Quinine. By A. CLAUS (*J. pr. Chem.* [2], **46**, 336—351).—This is a polemical paper, dealing with Grimaux's paper on quinine methiodides (Abstr., 1892, 1363).

Molecular Transformation of Cinchonine. By G. PUM (*Monatsh.*, **13**, 676—690; compare Abstr., 1892, 514; Lippmann and Fleissner, *ibid.*, 81; and Skraup, *ibid.*, 83).—The author has repeated, on a larger scale, the investigation of the products formed by decomposing trihydriodocinchonine with alcoholic potash and with silver nitrate respectively. He finds that in the first case cinchonine and isocinchonine are produced, whilst in the second, isocinchonine and *β-cinchonine* result from the decomposition.

β-Cinchonine melts at 250—252°, and forms a trihydriodo-derivative, $C_{19}H_{22}N_2O,3HI$, which melts at 228—229°, and is resolved by potash or silver nitrate into *β*-cinchonine and a small quantity of isocinchonine.

Trihydriodoisocinchonine, $C_{19}H_{22}N_2O,3HI$, melts at 227—229°, and is converted by alcoholic ammonia into dihydriodoisocinchonine, $C_{19}H_{22}N_2O,2HI$, which melts at 192—193°. When heated with

alcoholic potash, it is resolved into a mixture of isocinchonine and γ-cinchonine. The latter crystallises from absolute alcohol in small, transparent needles, melts at 235—236°, and forms an anhydrous, crystalline platinochloride.

β-Cinchonine and γ-cinchonine, or one of them, is, in all probability, identical with the optically active isomeride or isomerides of cinchonine isolated by Jungfleisch and Leger. G. T. M.

Coca Leaves. By C. Liebermann (*Annalen*, **272**, 238—242).—A polemical paper in reply to Hesse (this vol., i, 57).

Geoffroya Barks. By O. Hiller-Bombien (*Arch. Pharm.*, **230**, 513—548).—The barks known under the above name, including cabbage-tree bark and worm bark, were employed medicinally as anthelmintics about the end of the last century, but are now practically obsolete.

Hüttenschmid, in 1824 (and, later, Overduin and also Winkler), isolated an alkaloïd, *surinamine*, or *geoffroyine*, from true Geoffroya bark.

Geoffroyine (*methyltyrosine?*), $C_{10}H_{13}NO_3$, occurs in geoffroya bark, and is identical with rhatanine obtained by Ruge, in 1854, from rhatany extract, and with angeline, obtained by Gintl, in 1869, from the resin of the *Ferreia spectabilis*. The same alkaloïd is also present in various species of andira bark, and the author, therefore, proposes to adopt the name *andirine* in preference to those above given.

The alkaloïd is isolated by repeatedly extracting the bark with boiling water and evaporating the combined extracts, when a brown, hygroscopic mass remains. This is treated with hydrochloric acid, the solution filtered from the insoluble impurities, and the filtrate neutralised, when, if the solution be dilute, the alkaloïd separates in large, white crystals. This operation is repeated until the compound is pure. It is tasteless, its solution has a neutral reaction and is optically inactive, and, when the compound is allowed to remain with nitric acid (sp. gr. 1·4) for three days, it is converted, for the most part, into picric acid. It is soluble in 200 parts of boiling water, and in 695 parts of cold; also in 15,000 parts of absolute alcohol and in 914 parts of glacial acetic acid, but quite insoluble in benzene, ether, light petroleum, and several other solvents. Heated in a capillary tube, the compound melts at 233°, but its melting point is found to be 257° (corr.) when the determination is made by Dragendorff's method (*Pflanzenanalyse*, 1882, p. 13). The *hydrochloride* and *sulphate* are dissociated by water, and the free base is obtained when the alkaloïd is dissolved in glacial acetic acid and the solution evaporated. The *copper* salt, $(C_{10}H_{12}NO_3)_2Cu$, crystallises in anhydrous, microscopic, violet needles, and is sparingly soluble in water; a silver salt could not be prepared, as a solution of the base is reduced by silver oxide. When bromine is added to an aqueous solution of the base, the *dibromide*, $C_{10}H_{11}Br_2NO_3$, separates as a yellow, curdy precipitate, soluble in alcohol, chloroform, and aqueous ammonia. If the alkaloïd is boiled with acetic anhydride, an acetyl derivative is formed, but it

remains unaltered when heated in a sealed tube at 80° with methyl iodide.

The alkaloïd dissolves in concentrated sulphuric acid, forming a colourless solution which becomes brown on heating; an acid solution of vanadium sulphate gives a violet coloration, and, when the compound is evaporated with nitric acid, the residue gives a brick-red coloration with potassium hydroxide. On mixing the compound with water, and then adding nitric acid drop by drop, until it dissolves, and subsequently heating, a yellowish-red solution is obtained, which changes to bluish-violet, and finally becomes green with a reddish fluorescence. The alkaloïd dissolves in Millon's reagent, forming a dark red solution exhibiting an absorption of the spectrum from lines D to H. To detect the alkaloïd in a sample of bark, the latter is boiled with water, treated with basic lead acetate, and the filtrate, after removal of the lead, warmed with Millon's reagent, when a red coloration is produced, and subsequently a precipitate. A. R. L.

Ptomaïnes from the Urine in Erysipelas and Puerperal Fever. By A. B. Griffiths (*Compt. rend.*, **115**, 667—669).—The urine of erysipelas patients yields a ptomaïne which crystallises in white lamellæ belonging to the rhombic system; it is soluble in water, and has a feebly alkaline reaction. With mercuric chloride, it yields a flocculent precipitate; with zinc chloride, a granular precipitate, partially soluble with decomposition when heated; with Nessler's reagent, a green precipitate; with picric acid, a yellow precipitate; with gold chloride, a yellow precipitate; and precipitates also with phosphomolybdic, phosphotungstic, and tannic acids. This ptomaïne has the composition $C_{11}H_{13}NO_3$, and the author calls it *erysipeline*; it is highly poisonous, and produces high fever, resulting in death in a few hours. It does not occur in normal urine.

The urine of patients suffering from puerperal fever yields a white, crystalline ptomaïne of the composition $C_{23}H_{19}NO_2$, which is not found in normal urine. It forms a crystallisable hydrochloride and aurochloride, yields a red precipitate with tannin, a yellow precipitate with picric acid, and a brownish precipitate with phosphomolybdic acid; it is also precipitated by Nessler's solution. This ptomaïne is highly poisonous. C. H. B.

Preparation and Properties of Fibroïn. By L. Vignon (*Compt. rend.*, **115**, 613—615).—The statements of various chemists as to the proportion of fibroïn obtainable from raw silk differ very widely, and the author has therefore reinvestigated the matter.

10 grams of raw silk were boiled for 30 minutes with a solution of 150 grams of neutral white soap in 1500 c.c. of water, well washed, and then boiled for 20 minutes with a second similar quantity of soap solution. After this treatment, it was well washed with water, then with water acidified with hydrochloric acid, again with pure water, and, finally, with alcohol of 90°. In this way, 75 per cent. of fibroïn is obtained as a very brilliant, white, soft, tenacious, and elastic substance of sp. gr. about 1·34. Its percentage composition is C, 48·3;

H, 6·5; N, 19·2; O, 26·0 = 100·0, and it contains only 0·01 per cent. of ash.

When added to hydrochloric acid of 22°, fibroïn at first dissolves rapidly, but, as its proportion increases, it forms a viscous, transparent mass, exactly similar to the silk in the gland of the silkworm. A solution in concentrated hydrochloric acid is strongly lævogyrate. Alcohol of 95° precipitates the fibroïn from hydrochloric acid solutions in a form closely resembling gelatinous silica, and when dried at the ordinary temperature, it resembles dry albumin. Although it has lost its lustre, it retains its original composition, sp. gr., optical activity, and power of combining with colouring matters.

C. H. B.

Turacin. By A. H. Church (*Proc. Roy. Soc.*, **51**, 399—400).—Turacin, a definite, organic pigment, containing, as an essential constituent, about 7 per cent. of copper, occurs constantly in all the 18 known species of the three genera *Turacus*, *Gallirex*, and *Musophaga*, but is absent from the seven species included in the three remaining genera of the family *Musophagidæ*, namely, *Corythæola*, *Schizorhis*, and *Gymnoschizorhis*.

In alkaline solutions, turacin shows an absorption spectrum consisting of the two dark bands previously described (*Phil. Trans.*, 159, 627—636), and a faint, broad band, λ 496 to λ 475. Isolated turacin in ammoniacal solution shows these three bands and also a fourth, a narrow band extending from λ 605 to λ 589. The last band is probably due to the presence of traces of the green alteration product of turacin, which is probably identical with Krukenberg's *turacoverdin*. The ammoniacal solution remains unchanged, even after so long a period as 23 years.

Dry turacin, when suddenly and strongly heated, yields a volatile red derivative containing copper; it is insoluble in dilute ammonia solution, but dissolves in, and can be crystallised from, ether. When heated at the boiling point of mercury, dry turacin gives off no visible vapour, but is profoundly altered, becomes black, and insoluble in alkaline solutions, and gives off no vapours when strongly heated.

Turacin has the composition C, 53·69; H, 4·60; Cu, 7·01; N, 6·96; O, 27·74; but, although these numbers agree closely with those required by the formula $C_{82}H_{81}Cu_2N_9O_{32}$, the author does not attach very great weight to the results.

In some respects, turacin is analogous to hæmatin, and, when treated with sulphuric acid, it yields a coloured derivative *turacoporphyrin*, the spectra of which, in both acid and alkaline solutions, closely resembles those of hæmatoporphyrin. Turacoporphyrin, however, contains copper, whilst hæmatoporphyrin is free from iron.

C. H. B.

Organic Chemistry.

Graphochemistry of Compounds $C_nH_mO_p$. By E. NICKEL (*Zeit. physikal. Chem.*, **10**, 621—637; compare Abstr., 1892, 1158).—If p in the general formula $C_nH_mO_p$ is made equal to unity, and the percentage amounts of carbon and hydrogen are tabulated on rectangular axes, it is easy to define a field within which the composition of all compounds $C_nH_mO_p$ must lie, the limits in the various directions being given by the substances C, CH_4, CO_2, CH_4O, $C(OH)_4$, and H_2O. The interpretations of the different lines and pencils of rays obtained in the diagram are interesting, and are fully discussed by the author. Applications are made to the study of the possible decompositions of the substances without extraneous material being involved, and to the relation of composition to vapour density.

J. W.

Carbon Chloriodide. By A. BESSON (*Compt. rend.*, **115**, 1078—1079).—Carbon tetrachloride, mixed with its own weight of dry carbon bisulphide, is cooled to 0°, and successive small quantities of iodine are added, care being taken to avoid access of air and to keep the carbon tetrachloride in large excess. After two or three days, the excess of carbon tetrachloride and the carbon bisulphide are distilled off, after treatment with a dilute solution of an alkali. The fraction boiling above 142° is purified by treatment with a solution of an alkali and distillation in a vacuum. The product is *carbon trichloriodide*, CCl_3I, a colourless liquid with an aromatic odour and an irritating vapour; it solidifies at a low temperature, and melts at −19°; it boils at 142°, with partial decomposition in presence of air or an inert gas, but distils without change in a vacuum; sp. gr. at 17° = 2·36. In presence of air, or even of an inert gas, it decomposes at the ordinary temperature with separation of iodine and formation of carbon hexachloride, C_2Cl_6, and the change, which seems to reach a limit after a time, is promoted by exposure to light. In contact with mercury, decomposition is complete after a few hours.

C. H. B.

Reaction between Ferric Salts and Soluble Thiocyanates. By G. KRÜSS and H. MORAHT (*Zeit. anorg. Chem.*, **1**, 399—404).—The authors confirm the results obtained by Magnanini (Abstr., 1891, 1150), that in dilute solutions the addition of 12 mols. of a soluble thiocyanate to 1 mol. of a ferric salt does not suffice to convert the whole of the iron into the well-known red compound, and to produce the maximum coloration. In view of their former experiments (Abstr., 1889, 1129), they still regard the reaction as taking place in accordance with the equation $FeCl_3 + 12KCNS = Fe(CNS)_3,9KCNS + 3KCl$; but in order to realise the reaction in dilute solution, it is necessary, perhaps owing to electrolytic dissociation, that the thiocyanate should be present in excess.

H. C.

Action of Anhydrous Hydrogen Fluoride on Alcohols. By M. MESLANS (*Compt. rend.*, **115**, 1080—1082).—Anhydrous hydrogen fluoride has no action on absolute alcohol below 130°. At 140°, after six hours, about 2 per cent. of the alcohol is etherified; at 170°, 20 per cent. of the maximum possible change takes place. The best temperature is 210—220°, and, by using 4 mols. of the acid to 1 mol. of the alcohol, about 33 per cent. of the alcohol is etherified in three hours, and several litres of gaseous ethyl fluoride can be collected. Propyl and isopropyl alcohols and their homologues, under the same conditions, yield large quantities of the corresponding alkyl fluorides. The reacting substances are heated together in a copper tube, lined with platinum, and fitted with a screw-tap and a delivery tube by means of which the gas can be allowed to escape. C. H. B.

Rotatory Power of Sugars. By I. I. KANONNIKOFF (*J. Russ. Chem. Soc.*, **23**, 367—375).—In general, when two optically active sugars are mixed in molecular proportion, in solution, the specific rotatory power of the mixture is the mean of that of the components. There are exceptions to this rule, however, as the following table shows:—

	$[\alpha]_D$.	
	Found.	Calculated.
1 mol. dextrose + 1 mol. levulose.....	− 9·85°	−19·97°
1 mol. „ + 2 mols. „	−44·91	−44·97
1 mol. „ + 3 mols. „	−57·29	−57·41
2 mols. „ + 1 mol. „	+ 9·68	+ 4·99
3 mols. „ + 1 mol. „	+17·52	+17·47

The author attributes these discrepancies to the mutual action of the components of the mixture. J. W.

Formation of Ethereal Salts of Benzoic acid from Alcohols and Carbohydrates. By A. PANORMOFF (*J. Russ. Chem. Soc.*, **23**, 375—382).—1 part of a polyatomic alcohol or carbohydrate was added to 6 parts of benzoic chloride and 48 parts of an 18—20 per cent. solution of soda. The mixture was shaken for about an hour at 0°, allowed to remain over night, and the precipitate which separated from the liquid was washed with water until it showed an acid reaction. It was then crystallised from 95 per cent. alcohol until the melting point was constant.

The following benzoates were prepared in this way:—

From *dextrose*, $C_6H_7O_6Bz_5$, amorphous, m. p. 178°.
From *levulose*, $C_6H_7O_6Bz_5$, amorphous, m. p. 78—79°.
From *galactose*, $C_6H_7O_6Bz_5$, m. p. 78—82°.
From *cane sugar*, $C_{12}H_{15}O_{11}Bz_7$, amorphous, m. p. 98°.
From *milk sugar*, $C_{12}H_{15}O_{11}Bz_7$, long crystals, m. p. 200°.

From *maltose*, $C_{12}H_{13}O_{11}Bz_7$, amorphous, m. p. 109—115°.

From *glycogen* (from liver and muscle), $C_6H_8O_5Bz_2$, amorphous, turns brown at 187°, melts at 195°.

From *mannitol*, $C_6H_8O_6Bz_6$, recrystallised from acetic anhydride, fine needles, m. p. 149°. J. W.

Conversion of Starch into Sugar by means of Blood Serum. By F. RÖHMANN (*Ber.*, **25**, 3654—3657).—The author has fully identified the sugar formed by the action of blood serum on potato starch as being dextrose; the yield of the sodium chloride derivative is 40 grams from 110 grams of starch. Maltose appears to be formed at the commencement of the operation. Soluble starch and dextrin are also produced, the quantities depending on the length of time the fermentation is allowed to proceed. The dextrin may be separated into two portions by treatment with methyl alcohol; one of these, achroödextrin, is not acted on by iodine, whilst the other is coloured brown. J. B. T.

Chemical Conditions of the Action of Diastases. By J. EFFRONT (*Compt. rend.*, **115**, 1324—1326).—The saccharifying power of amylase, glycase, and the soluble ferment of *Aspergillus oryzæ*, or a mixture of them, can be increased in the proportion of 1 to 10 by the addition of aluminium salts, phosphates, asparagine, and certain albumins. In the case of aluminum acetate, ammonium phosphate, and asparagine, the effect is the same whether the salt is first mixed with the diastase and the starch added, or is mixed with the starch and the diastase added; but with calcium phosphate and with alum, the results differ according to the mode of procedure. The influence of these chemical compounds is independent of the temperature at which saccharification takes place, but decreases as the quantity of sugar increases, and disappears when the proportion of sugar reaches 60 per cent., a result due to the nature of the different dextrins formed during the conversion of starch into sugar.

It is noteworthy that the substances that promote the action of the diastases are also those which promote the action of organised ferments. The action of the salts is probably the same in both cases, and it seems likely that their effect is due to the formation of intermediate compounds, and, consequently, that their mode of action is analogous to that of metallic salts in Friedel and Craft's synthesis. C. H. B.

Amidoacetaldehyde (Ethanalamine). By E. FISCHER (*Ber.*, **26**, 92—98).—*Amidoacetaldehyde hydrochloride* is obtained by adding an aqueous solution of amidoacetal, drop by drop, to well-cooled hydrochloric acid (sp. gr. = 1·19), and after allowing the mixture to remain at the ordinary temperature 4—5 hours, distilling it in a vacuum at 40°. The hydrochloride remains as a colourless syrup, which deliquesces on exposure to air and has not been obtained crystalline. The *hydrobromide* is prepared in the same way and resembles the hydrochloride. The *platinochloride*, $(CHO{\cdot}CH_2{\cdot}NH_2)_2,H_2PtCl_6 + 2C_2H_6O$, is prepared in alcoholic solution; it crystallises in yellow, microscopic needles and decomposes at 80—90°. When prepared in

methyl alcoholic solution, it crystallises in small, six-sided, yellow tablets, containing 2 mols. of methyl alcohol.

Amidoacetaldehyde is so unstable that it has not yet been isolated. When the hydrochloride is warmed with dilute sodium hydroxide, ammonia is evolved; when treated with a cold solution of barium hydroxide, a gelatinous mass is obtained. The alkaline solutions energetically reduce Fehling's solution and ammoniacal silver solutions. The hydrochloride is converted into amidoacetic acid when oxidised with bromine, and into glyoxalphenylosazone when treated with phenylhydrazine acetate.

Glyoxalphenylosazone has been obtained by crystallisation from ether in well-formed crystals, which melt at 177° (179°, corr.) and belong to the monoclinic system, $a : b : c = 0{\cdot}8638 : 1 : 1{\cdot}9029$; $\beta = 72° 36' 37''$. E. C. R.

Thiocyanacetone. By J. Tcherniac (*Ber.*, **25**, 3648; compare Abstr., 1892, 1425).—A reply to Hantzsch's criticism (this vol., i, 64) of the author's previous work on this subject. J. B. T.

Constitution of Isomeric Aliphatic Oximes. By G. Minunni (*Gazzetta*, **22**, ii, 431—438).—This paper is a reply to the objections raised by Hantzsch (Abstr., 1892, 1268) and V. Meyer (Abstr., 1892, 932) to the author's explanation of the isomerism of the oximes; no new facts are brought forward. W. J. P.

Perchlorethyl Chloroformate and Trichloromethyl Trichloracetate. By R. Anschütz and W. O. Emery (*Annalen*, **273**, 56—63; compare Müller, Abstr., 1890, 1095).—Trichloromethyl trichloracetate, $CCl_3{\cdot}COOCCl_3$, was prepared by chlorinating methyl trichloracetate at the ordinary temperature, and purified by repeated fractional distillation under reduced pressure; it is a colourless, crystalline compound, melts at 34°, and boils at 73—74° under a pressure of 10 mm., and at 191—192° under the ordinary atmospheric pressure; its sp. gr. = 1·67331 at 35°/4°.

Perchlorethyl chloroformate, $Cl{\cdot}COOC_2Cl_5$, obtained from ethyl chloroformate in a similar manner, forms transparent crystals, melts at 26—27°, and boils at 83—84° under a pressure of 10 mm., and at 209—210° under the ordinary atmospheric pressure; its sp. gr. = 1·73702 at 35°/4°.

These facts show that the two compounds are not identical, although, as was observed by Cloez (*Ann. Chim. Phys.* [3], **17**, 297), they are both decomposed by water, yielding hydrogen chloride, carbonic anhydride, and trichloracetic acid; this identity in behaviour can be explained by assuming that they are both converted into an intermediate product of the constitution $COCl{\cdot}O{\cdot}CO{\cdot}CCl_3$.

F. S. K.

Brom-additive Products of Angelic and Tiglic acids. By R. Fittig (*Annalen*, **273**, 127—132).—The author disputes the accuracy of some of Wislicenus' methods (this vol., i, 135) and results, and refuses to continue the discussion of the matters in question.

F. S. K.

New Unsaturated Fatty Acid. By Y. Shimoyama (*Chem. Centr.*, 1892, ii, 646; from *Apoth. Zeit.*, **7**, 453—454).—*Senecioic acid*, $C_4H_7{\cdot}COOH$, occurs in the rhizomes of the Japanese evergreen *Senecio Kämpferi*; it crystallises in odourless, colourless, silky needles or prisms, melts at 65°, and decomposes carbonates. The *silver* salt forms white, silky plates; the *calcium* salt, with $3H_2O$, needles, soluble in water. With bromine, in carbon bisulphide solution, it yields the *dibromide*, $C_5H_8Br_2O_2$, which forms colourless crystals melting at 107°. By the action of hydrobromic acid, saturated at 0°, it is converted into *hydrobromosenecioic acid*, $C_4H_6Br{\cdot}COOH$, which crystallises in colourless needles and melts at 71°. Nascent hydrogen does not act on senecioic acid. A. J. G.

Intramolecular Changes in Unsaturated Acids. By R. Fittig (*Ber.*, **26**, 40—49).—This paper contains a *résumé* of the work carried out on this subject by the author and his pupils, a full account of which will shortly be published.

The author previously observed (Abstr., 1891, 452) that certain $\beta\gamma$-unsaturated acids are converted by the action of boiling aqueous soda into the isomeric $\alpha\beta$-acids; a large number of other acids of the first-named class have now been examined, and the same rule has been found to hold good in every case; the conversion is, however, never complete, as the reverse reaction also takes place, and some β-hydroxy-acid is always formed by the union of the unsaturated acid with the elements of water. Hence a condition of equilibrium is eventually reached between the proportions of the three acids, the point of which probably depends on the concentration of the soda solution. The pure hydroxy-acids when treated alone with soda again lose water, and yield a mixture of the $\alpha\beta$- and $\beta\gamma$-unsaturated acids, the former being obtained in much larger quantity, and the $\alpha\beta$-acids themselves under the same conditions are partially converted into the $\beta\gamma$-acids. Whether all these reactions are caused by the primary formation of the β-hydroxy-acids, or whether the $\alpha\beta$-acids are first formed and then converted into the hydroxy-acids, is as yet uncertain.

The $\alpha\beta$-acids are distinguished from the $\beta\gamma$-acids by their higher melting points, and by the fact that dilute sulphuric acid, which converts the $\beta\gamma$-acids in a few minutes into the hydroxy-acids, is without action on them; this forms, therefore, a ready and accurate method of separating the members of the two series. The whole of the evidence is against the view that the first series are stereoisomerides of the second; thus both combine with bromine and hydrogen bromide, yielding different dibromides and monobromo-derivatives; the latter, when obtained from the $\beta\gamma$-acids, are readily converted by boiling water into lactones, whilst those from the $\alpha\beta$-acids yield unsaturated hydrocarbons and hydroxy-acids.

Allylacetic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, remains unaltered after boiling for several hours with concentrated alkali, whereas the isomeric ethylidenepropionic acid, $CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, is converted into an acid which is probably propylideneacetic acid, $CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$. Allylmalonic acid is also indifferent towards alkali.

The conversion of the lactonic acids (paraconic acids) into the unsaturated dicarboxylic acids homologous with itaconic, citraconic, and mesaconic acids has also been closely followed in a large number of cases, and the chemical and physical properties of these acids were found to be largely reproduced in their homologues. All the citraconic acids are very readily soluble in water, and melt below or slightly above 100°, splitting up at the same time into anhydride and water; the solubility of the itaconic and mesaconic acids, on the other hand, decreases with an increasing number of carbon atoms. The itaconic acids melt only with simultaneous decomposition, but the mesaconic acids, although possessing the highest melting points, can be melted without decomposition; the latter are identical with the so-called oxytetric and oxypentic acids (compare Abstr., 1891, 1188).

The conversion of the itaconic into the citraconic acids is brought about by dry distillation, some of the itaconic anhydride passing over at the same time, the quantity of the latter being increased if the distillation is carried out in a vacuum. In the case of teraconic acid (dimethylitaconic acid), the itaconic anhydride is then exclusively formed, but at the atmospheric pressure some of the citraconic anhydride is also formed. To separate the citraconic acids, the distillate is boiled with water, when the citraconic anhydride distils over with the water.

Phenylitaconic acid shows a somewhat anomalous behaviour, inasmuch as, even when distilled in a vacuum, it undergoes a far-reaching decomposition; if simply melted in a vacuum, however, a little citraconic anhydride is formed, together with the itaconic anhydride, and may be extracted with carbon bisulphide, in which the latter is insoluble. If it be again heated to its melting point (160—165°), which is approximately the same as the temperature at which it is formed, it is reconverted almost completely into the itaconic anhydride.

The conversion of the citraconic into the mesaconic acids is best brought about by the action of a small quantity of bromine on a chloroform solution in bright daylight or sunlight; the change takes place in a few minutes, the mesaconic acid separating out in crystals, which, after washing with chloroform, are pure. This method is also the most suitable for the preparation of mesaconic acid itself from citraconic acid, with the modification that the latter is dissolved in ether. That the hydrogen bromide formed in the reaction is not the agent which effects the change, is shown by the fact that hydrogen bromide alone is incapable of bringing it about, and the explanation given by Wislicenus for this change is, therefore, no longer tenable. In absence of light and water, bromine acts only very slowly on citraconic acid, the chief product being then citradibromopyrotartaric acid.

The itaconic acids are only attacked with difficulty by nascent hydrogen, the mesaconic acids more readily, and the citraconic acids the most easily; in all cases the same succinic acid is obtained from all three isomerides. When heated with concentrated hydrochloric or hydrobromic acid, and subsequently boiled with water, the itaconic acids are converted into the paraconic acids from which they were obtained, except in the case of isopropylitaconic acid, which, in place

of the original isopropylparaconic acid, $\begin{matrix}\mathrm{COOH{\cdot}CH-CH_2}\\ \mathrm{CHPr^{\beta}{\cdot}O}\end{matrix}\!>\!\mathrm{CO}$, yields an isomeric lactonic acid, which has probably the constitutional formula $\begin{matrix}\mathrm{CMe_2{\cdot}CH_2}\\ \mathrm{O\text{——}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}CH_2{\cdot}COOH}$, as it is also obtained by oxidising isobutylsuccinic acid with alkaline permanganate. The change is similar to that which takes place in preparing tertiary butyl alcohol from isobutyl alcohol.

The itaconic acids are not altered by boiling with soda, except in so far as a small quantity of hydroxy-acid is formed, whilst the citraconic and mesaconic acids are converted into the itaconic acids, the former more quickly than the latter. In no case was the formation of citraconic acids from either of the other two series observed. According to Delisle (Abstr., 1892, 297), citraconic acid is under these conditions converted into mesaconic acid, and the author has confirmed this statement; the exception is not due to the abnormal behaviour of citraconic acid, for this is converted as usual into itaconic acid; the latter is, however, itself converted by boiling soda into mesaconic acid. H. G. C.

Diglycollic acid and Thiodiglycollic acid. By R. Anschütz and F. Biernaux (*Annalen*, **273**, 64—73; compare Abstr., 1891, 177). —*Diglycollic chloride*, $\mathrm{O(CH_2{\cdot}COCl)_2}$, is formed when diglycollic acid is treated with phosphorus pentachloride (2 mols.); it is a colourless, oily, highly-refractive liquid, boils at 116° under a pressure of about 12 mm., and is immediately decomposed by water.

Methyl diglycollate, $\mathrm{O(CH_2{\cdot}COOMe)_2}$, prepared by treating the chloride with methyl alcohol, crystallises in lustrous, colourless plates, and melts at 36°.

Diglycollanil, $\mathrm{O\!<\!\begin{matrix}CH_2{\cdot}CO\\ CH_2{\cdot}CO\end{matrix}\!>\!NPh}$, is obtained when diglycollanilic acid (*loc. cit.*) is treated with excess of acetic chloride; it crystallises in small prisms melting at 111°.

Diglycollanilide, $\mathrm{O(CH_2{\cdot}CO{\cdot}NHPh)_2}$, prepared by treating a well-cooled ethereal solution of the chloride with aniline, crystallises in colourless needles, and melts at 152°.

Thiodiglycollic anhydride, $\mathrm{S\!<\!\begin{matrix}CH_2{\cdot}CO\\ CH_2{\cdot}CO\end{matrix}\!>\!O}$, is produced when the acid is boiled with acetic chloride, or distilled under reduced pressure; it crystallises in colourless needles, melts at 102°, and boils at 158°, under a pressure of about 10 mm.; it is very readily decomposed by water. The *chloride* $\mathrm{S(CH_2{\cdot}COCl)_2}$ was prepared.

Methyl thiodiglycollate, $\mathrm{S(CH_2{\cdot}COOMe)_2}$, is a colourless, highly refractive liquid, boiling at 135°, under a pressure of about 11 mm.

Thiodiglycollanilic acid, $\mathrm{NHPh{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}COOH}$, separates from boiling water in well-defined crystals melting at 103°.

Thiodiglycollparatolilic acid, $\mathrm{C_{11}H_{13}SNO_3}$, crystallises in colourless needles, and melts at 95°.

Thiodiglycollanilide, $\mathrm{S(CH_2{\cdot}CO{\cdot}NHPh)_2}$, crystallises in needles melting at 168°. F. S. K.

Action of Water on Bromosuccinic acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **23**, 339—343).—When a solution of bromosuccinic acid is allowed to remain at the ordinary temperature, no change takes place, but a solution of its potassium salt undergoes considerable decomposition in 24 hours under the same circumstances. The amount of decomposition was measured by the author by the increase in the acid titre of the solution, consequent on the formation of hydrobromic acid. When the acid or its potassium salt is heated at 100°, decomposition takes place, and is practically complete within 12 hours. The more dilute the solution, the more rapid is the decomposition. Hydrochloric acid does not greatly influence the speed of the reaction. The products of the action of water on bromosuccinic acid are inactive lactic acid and hydrobromic acid, fumaric acid not being formed, at least primarily. J. W.

Mixed Anhydrides of Hypochlorous and Analogous Acids. By T. Selivanoff (*Ber.*, **25**, 3617—3623).—The author proposes that chlorine, when present in a compound as the radicle of hypochlorous acid, be termed *chloryl;* thus he names the compound Ac·NHCl, chlorylacetamide.

Chlorylsuccinimide, $\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}\!\!>\!NCl$, is obtained by the action of hypochlorous acid on succinimide. It is a powerful oxidising agent. Primary and secondary alcohols are oxidised, but trimethylcarbinol is not attacked; it may be employed, therefore, to ascertain whether a given alcohol is tertiary or not. The presence of water is necessary to develop the oxidising powers of chlorylsuccinimide; thus a solution of chlorylsuccinimide in dry benzene is without action on potassium iodide, but if the smallest quantity of water is added, iodine is at once liberated; the imide is decomposed by warm water into succinimide and hypochlorous acid, the aqueous solution showing all the properties of hypochlorous acid. From these results, the author concludes that chlorylsuccinimide is an anhydride or amide of hypochlorous acid. Other similar acid amides containing chlorine, which the author has examined, behave like chlorylsuccinimide, and are considered to be anhydrides of hypochlorous acid.

The chlorine derivatives of amines, R:NHCl and $RNCl_2$, behave in a manner analogous to the derivatives of the acid amines, and when hydrolysed with dilute sulphuric acid yield hypochlorous acid; they also have chlorinating and oxidising properties. Thus, dichlorylethylamide, $EtNCl_2$, when treated with water, yields 2 mols. HClO.

Succinimide, when treated with chlorylacetamide, yields chlorylsuccinimide, which is an anhydride of hypochlorous acid, and, therefore, chlorylacetamide must be a similar anhydride. In this way, by acting on amines with chlorylacetamide or chlorylsuccinimide, the author has obtained the following compounds:—Dichlorylethylamide, chloryldiethylamide, chlorylpiperidine, $C_5H_{10}NCl$, chloryldipropylamide, and chloryldiisobutylamide. E. C. R.

Condensation of Ethyl Formate and Succinate. By F. Anderlini and E. Borisi (*Gazzetta*, **22**, ii, 439—442).—Ethyl formate

and succinate react in presence of potassium ethoxide free from potash, and the product, on suitable treatment, yields *ethyl formylsuccinate*, $C_9H_{11}O_5$; this may be purified by means of the solid compound which it forms with potassium carbonate, and which is decomposed by hydrochloric acid. The new substance is a colourless, limpid oil, which boils at 125—126° under 16 mm. pressure; it has a pleasing, ethereal odour, and is miscible in all proportions with alcohol or ether, but is insoluble in water. It gives a deep violet coloration with ferric chloride, and, on treatment with hydroxylamine hydrochloride and alkalis, it yields an oil, probably consisting of the corresponding *oxime*. W. J. P.

Ethyl Oxomalonate. By R. Anschütz and E. Parlato (*Ber.*, **25**, 3614—3617).—*Ethyl oxomalonate*, $CO(COOEt)_2$, is obtained by suspending dry barium mesoxalate in absolute alcohol and saturating the mixture with dry hydrogen chloride. It is a bright, greenish-yellow oil, of not unpleasant odour, boils at 100—101° under 14 mm. pressure, and has a sp. gr. = 1·1358 at 16°/16°. When treated with water, it is very easily converted into ethyl dihydroxymalonate, which melts at 57°.

Ethyl dihydroxymalonate cannot be distilled without decomposition; when heated under diminished pressure, it loses water at 40°, and is converted into ethyl oxomalonate; the water formed must, however, be carefully absorbed by phosphoric anhydride, otherwise ethyl dihydroxymalonate is reproduced.

Ethyl oxomalonate is also obtained by treating ethyl acetotartronate with the equivalent quantity of bromine, and distilling the product under diminished pressure. E. C. R.

Isomerism of Fumaric and Maleïc acids. By S. Tanatar (*Annalen*, **273**, 31—55).—Most of the experiments here described have been previously published (Abstr., 1890, 1238; 1891, 174, 175; 1892, 1304, *et seq.*).

When silver malonate is warmed with a 30 per cent. solution of dibromacetic acid, carbonic anhydride is evolved, and silver bromide is deposited; the solution then contains a small quantity of fumaric acid, a little maleïc acid, a crystalline acid of the composition $C_4H_6O_5$, and a liquid acid. The crystalline *acid*, $C_4H_6O_5$, melts at 70—80°, is hygroscopic, and optically inactive; it does not give fumaric acid when heated with water at 200°, or when boiled with hydrochloric acid, but when distilled under reduced pressure, it yields fumaric acid and a larger proportion of maleïc acid; its salts are amorphous. The liquid acid yields fumaric acid and larger quantities of maleïc acid on distillation under reduced pressure, and on prolonged boiling with hydrochloric acid it gives a little fumaric acid; it is inactive, and its salts are amorphous.

If levulinic acid has the constitution $CH_2<\begin{matrix}CH_2\\COO\end{matrix}>CMe{\cdot}OH$, as supposed by Anschütz, it is possible that it would have an abnormal heat of neutralisation; experiments showed that this was not the case. F. S. K.

Homologues of Citraconic, Itaconic, and Mesaconic acids. By V. Semenoff (*J. Russ. Chem. Soc.*, **23**, 430—443).—Ethylic ethylacetoacetate was treated with bromine (2 mols.) either without a solvent, in ethereal solution, or under water. The product, after removal of the excess of bromine (and of the ether in the second case), was treated with excess of alcoholic potash, distilled with steam, acidified, and again distilled with steam. The residual solution, after being filtered to remove tarry matter, was evaporated to a smaller bulk, when small, brownish crystals separated on cooling. The mother liquor was extracted with ether, and from the ethereal extract a further quantity of organic acid was obtained, which was added to the first crop of crystals. The total yield of crude acid was about 25—30 per cent.; this was dissolved in dilute nitric acid, and boiled until the brown colour disappeared. On cooling and recrystallisation from water, the acid was obtained in colourless crystals.

Methylmesaconic acid, $C_6H_8O_4$.—The acid thus prepared is sparingly soluble in cold water, but easily in hot water or in ether. When crystallised from a boiling aqueous solution, it resembles fumaric acid in external appearance. It sublimes in needles which melt at 195—196°, and the alkali salts are easily soluble both in hot and in cold water. The calcium salt, $CaC_6H_6O_4 + 3\frac{1}{2}H_2O$, crystallises sometimes in stellate clusters of prisms, sometimes in single crystals. At 160° it becomes yellow, but does not part with all its water below 180°. The barium salt, $BaC_6H_6O_4 + 1\frac{1}{2}H_2O$, is precipitated in a finely crystalline state from its aqueous solution on adding alcohol; from a cold solution it separates in nodules. On reduction with sodium amalgam, the acid yields ethylsuccinic acid melting at 99—99·5°.

Methylcitraconic acid, $C_6H_8O_4$.—19 grams of methylmesaconic acid was heated for 10 hours in a sealed tube at 105—110° with 42 grams of acetic chloride. From the product an anhydride was obtained distilling at 142° under 66 mm. pressure; this combined only slowly with cold water, but rapidly with hot water, giving a solution from which methylcitraconic acid crystallised in the form of large, transparent prisms. This acid is very soluble in water or ether, easily in boiling chloroform, slightly in benzene, and insoluble in light petroleum. It melts at 95—96°, and decomposes at a comparatively low temperature into anhydride and water. An aqueous solution of the free acid yields the anhydride as a heavy, yellow oil on evaporation. The calcium salt, $CaC_6H_6O_4 + H_2O$, is more soluble in cold than in boiling water; so, likewise, is the barium salt, which crystallises with $1\frac{1}{2}$ mol. H_2O in hot solution, and with 4 mols. H_2O from a cold solution. The silver salt may be obtained as a fine, crystalline powder by precipitation.

A concentrated solution of methylcitraconic acid, heated for 10 hours at 140—150°, deposits *methylitaconic acid*, $C_6H_8O_4$, on cooling; this is crystalline, melts at 165—166°, is more soluble in water than methylmesaconic, but less soluble than methylcitraconic acid, and crystallises from a cold solution in clusters of prisms or tables. The transformation of methylcitraconic acid into its isomeride may be effected in the absence of water by heating for 24 hours at 100°. The calcium salt, $CaC_6H_6O_4 + H_2O$, separates as small scales when its

cold aqueous solution is heated to boiling; and the silver salt crystallises from its boiling solution in rhombohedra.

When ethylic propylacetoacetate is brominated and the product treated with alcoholic potash, *ethylmesaconic acid*, $C_7H_{10}O_4$, is obtained; this crystallises in small, colourless scales, little soluble in cold water, but easily soluble in boiling water and in ether. When gently heated, it sublimes in small needles melting at 172·5—173°. The calcium and barium salts are more soluble in cold than in hot water, and the silver salt becomes red on exposure to light. On reducing with sodium amalgam, the acid yields propylsuccinic acid.

Ethylcitraconic acid, $C_7H_{10}O_4$, is formed from ethylmesaconic acid similarly to the methyl compound. The anhydride boils at 152° under a pressure of 68 mm., and the acid melts at 92—94°, and crystallises from water in the form of large, transparent prisms. The *calcium* and *barium* salts, which crystallise with 1 mol. H_2O and $\frac{1}{2}$ mol. H_2O respectively, separate from their concentrated, cold aqueous solutions on boiling. The silver salt is an insoluble, crystalline powder.

Ethylcitraconic acid in aqueous solution is transformed into *ethylitaconic acid*, $C_7H_{10}O_4$, at 150°; this is less soluble in water than either of its isomerides, and melts at 164—165° after softening. The calcium salt, $CaC_7H_8O_4 + H_2O$, separates from the boiling solution in flocks; the silver salt, which is also flocculent, is soluble in water and blackens on boiling. Ethylitaconic acid, unlike its isomerides, is only reduced by sodium amalgam with great difficulty. J. W.

Stereochemical Notation: a Reply to Colson. By C. Friedel (*Compt. rend.*, **115**, 994—995).—The author points out that Colson (this vol., ii, 105, 106) has misrepresented Van't Hoff's schematic formulæ for the two active tartaric acids, probably through incorrectly translating the abridged notation. The author considers that the symbolic tetrahedron is much less likely to lead to confusion than any other method of representing optically active compounds.

C. H. B.

Constitution of Leucine. By E. Schulze (*Ber.*, **26**, 56—57).—The author, in conjunction with Likiernik (Abstr., 1891, 681), has shown that the inactive leucine obtained by them from conglutin is converted by nitrous acid into a hydroxy-acid which is identical with the acid obtained in a similar manner from the synthetical α-amidoisobutylacetic acid. It should also be identical with the leucic acid of Erlenmeyer and Sigl (*Ber.*, **7**, 1109), but the authors found for their acid the melting point 52°, instead of 54—56°, as given by Erlenmeyer. After more careful purification, the author has now obtained his hydroxycaproic acid in crystals melting at 54·5°.

The action of *Penicillium glaucum* on the synthetical α-amidoisobutylacetic acid has again been investigated, the results agreeing with those previously obtained. The α-amido-acid obtained from fermentation caproic acid has also been subjected to the action of the same organism, but was found to give a solution of higher lævorotatory power than the synthetical acid, which must therefore be different from the leucine obtained by the author. H. G. C.

Preparation of Zinc Ethide. By M. Fileti and A. Cantalupo (*Gazzetta*, **22**, ii, 387—388).—The authors prepare zinc ethide by exposing a mixture of zinc turnings, ethyl iodide, and a little zinc ethide to diffused light in an atmosphere of carbonic anhydride; after a week's time, all the ethyl iodide disappears, and on distilling the product in an atmosphere of carbonic anhydride, almost the theoretical yield of zinc ethide is obtained. W. J. P.

Derivatives of Nononaphthene. By M. Konovaloff (*J. Russ. Chem. Soc.*, **23**, 446—451).—In the preparation of the monochloro-derivative of nononaphthene (b. p. 135—137°) there is formed a considerable quantity of a substance heavier than water and volatile with steam. This substance the author fractionated, first under reduced pressure, and then at atmospheric pressure in a current of carbonic anhydride; in this way, he succeeded in isolating a fraction boiling between 230° and 235°, which had the composition $C_9H_{16}Cl_2$. This dichloride has the sp. gr. 1·1035 at 0°/0°, and does not solidify in a mixture of ice and salt. Aniline abstracts hydrogen chloride from the molecule only at a very high temperature, and even then incompletely. By heating, however, with dry sodium acetate (2 mols.) and glacial acetic acid (2 mols.) for five hours at 200°, a considerable quantity of unsaturated hydrocarbon was obtained, which was dried and fractionated over sodium; all the fractions were colourless, but rapidly became brown on exposure to air. The lower fractions were volatile with steam, and boiled chiefly between 139° and 152°. The portion boiling at 139—141° gave numbers, on analysis, closely approximating to those required by the formula C_9H_{14}. This hydrocarbon, in acetic acid solution, is at once attacked by bromine at a low temperature, with formation of a crystalline powder easily soluble in alcohol and ethyl acetate, soluble with difficulty in ether, and almost insoluble in boiling benzene. The crystals from a weak acetic acid solution form long, silky needles. The bromide rapidly decomposes in the air, a tarry mass being formed; and the dry substance is carbonised at 70°.

The fraction boiling at 305—315° has also the formula C_9H_{14}, but freezing point determinations in benzene give a molecular weight nearly corresponding with the formula $(C_9H_{14})_2$. It is a heavy oil, and forms a tarry mass both with bromine and with dry hydrogen chloride. J. W.

Action of Nitric and Nitrous acids on certain Organic Substances. By A. Angeli (*Gazzetta*, **22**, ii, 325—340; compare Abstr., 1892, 447 and 1198).—Cramer's demonstration (Abstr., 1892, 699) that the substance obtained by Pröpper by the action of nitric acid on ethyl acetoacetate contains the group $\begin{matrix}-C{:}N{\cdot}O\\ |\\ -C{:}N{\cdot}O\end{matrix}$, gives weight to the author's opinion that eulyte (*Gazzetta*, **21**, ii, 32) contains this group. The author was unable to obtain an analogous compound by the action of nitric acid on bromocitraconic acid.

The action of nitric acid on phenacylacetone would be expected to

yield a substance similar to eulyte, as does acetonylacetone (Abstr., 1891, 890); this, however, is not the case, a *substance* of the composition $C_{21}H_{18}N_4O_{11}$ being formed. This crystallises in white scales, melts at 210°, and is insoluble in alkalis and alkaline carbonates.

Ethyl isodehydracetate reacts readily with fuming nitric acid, yielding a *nitro*-derivative (?) of the composition $C_9H_9NO_5$, which separates from benzene in magnificent, yellowish crystals melting at 98°. It is insoluble in alkali carbonates, but dissolves slowly in alkalis.

The action of nitrous acid on a large number of substances is discussed, and several of the products obtained by its action on aromatic compounds are described.

Isosafrole yields a *nitrosite*, $CH_2{:}O_2{:}C_6H_3{\cdot}C_3H_5N_2O_3$, with nitrous acid; it forms white, microscopic crystals melting with decomposition at about 130°. It is almost insoluble in most solvents, and its *anhydride*, $CH_2{:}O_2{:}C_6H_3{\cdot}C_3H_3N_2O_2$, forms yellow needles melting at 124° without decomposition; this is very soluble in benzene, but only sparingly in alcohol. It dissolves in sulphuric acid, and is precipitated unchanged with water.

Methyleugenol nitrosite anhydride, $C_6H_3(OMe)_2{\cdot}C_3H_3N_2O_3$, forms yellow needles melting at 118°, and closely resembles the preceding compound.

Isoapiole nitrosite, $CH_2{:}O_2{:}C_6H(OMe_2){\cdot}C_3H_3N_2O_3$, melts at about 132°, whilst its *anhydride* forms yellow needles melting at 170°.

Isobutenylphenyl nitrosite, $C_6H_5{\cdot}C_4H_7N_2O_3$, forms beautiful, colourless needles melting at 112° with decomposition.

The author concludes that the action of nitrous acid on unsaturated aromatic substances affords a means of ascertaining whether a double bond in the side chain is contiguous to the aromatic nucleus or not; with such substances a nitrosite cannot be prepared, whilst if the unsaturated side chain be united to the nucleus by a single bond, a nitrosite will be formed on treatment with nitrous acid.

W. J. P.

Action of Hydrogen Peroxide on Aniline. By E. Schunck and L. Marchlewski (*Ber.*, **25**, 3574—3577).—The lake obtained by Leeds by the action of hydrogen peroxide on aniline was regarded by Schunck and Brebner as dianilidobenzoquinoneanilide. In confirmation of this view, the authors now find that when aniline is heated on the water-bath with a solution of hydrogen peroxide in dilute acetic acid, ammonia, azobenzene, and dianilidoquinoneanilide are the products. When, however, a solution of hydrogen peroxide in dilute hydrochloric acid is employed, a compound is formed which perhaps is an induline. In view of the possibility that azobenzene is the primary product of the action, and to throw light on the formation of the anilidoquinone, the authors examined the reaction between azobenzene and a boiling acid solution of hydrogen peroxide, without, however, recognising with certainty the production of quinone. It may, therefore, be assumed that the azobenzene, at the moment of its formation, reacts with the hydrogen peroxide, giving rise to quinone, which then acts on the excess of aniline.

A. R. L.

Paraxylidine. By R. MICHAEL (*Ber.*, **26**, 39).—When pure paraxylidine is exposed to a very low temperature for a long time, it crystallises in large, colourless plates, frequently united in twins. It melts at 15·5°, and boils at 213·5° (uncorr.) under 762 mm. pressure. The *acetyl* compound melts at 139·5°. H. G. C.

Some Nitro- and Amido-benzylated Bases. By E. LELLMANN and N. MAYER (*Ber.*, **25**, 3581—3586).—*Orthodinitrodibenzylparatoluidine*, $C_6H_4Me{\cdot}N(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, is prepared by boiling an alcoholic solution of orthonitrobenzyl chloride (2 mols.) and paratoluidine for half an hour, evaporating the alcohol, and heating the residue with aqueous sodium carbonate for some hours at 110—120°; it crystallises in yellow needles, melts at 160°, and is sparingly soluble in alcohol and ether. *Paradinitrodibenzylparatoluidine* forms yellow crystals, and melts at 189°. Only one nitrobenzyl residue can be introduced into orthotoluidine. *Orthonitrobenzylorthotoluidine*,

$$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

melts at 96°; *paranitrobenzylorthotoluidine* crystallises in bright red needles, and melts at 93°; whilst *paranitrobenzylparatoluidine* forms yellow crystals, and melts at 68°.

Orthodinitrodibenzylmetadiamidobenzene, $C_6H_4(NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, is prepared by heating an alcoholic solution of 1 : 2-diamidobenzene hydrochloride (1 mol.) and orthonitrobenzyl chloride (2 mols.) on the water-bath; it separates in green crystals, and melts at 134°. *Orthodinitrodibenzylorthodiamidotoluene* forms red crystals, and melts at 129°.

Orthonitrobenzylmetamidophenyl orthonitrobenzyl ether,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

is obtained by heating metamidophenol (1 mol.) with orthonitrobenzyl chloride (2 mols.) and sodium acetate (2 mols.) in alcoholic solution; it forms dark brown crystals, melts at 190°, and is insoluble in alkalis.

Orthonitrobenzyl orthonitrophenol ether, $NO_2{\cdot}C_6H_4{\cdot}OCH_2{\cdot}C_6H_4{\cdot}NO_2$, is formed by heating equivalent quantities of potassium orthonitrophenol and orthonitrobenzyl chloride, dissolved in alcohol, on the water-bath; it crystallises in colourless needles, and melts at 154°. None of the new dinitro-derivatives described above could be converted into azo-compounds by treating them with alkaline stannous chloride.

Orthodiamidodibenzylaniline, $NPh(CH_2{\cdot}C_6H_4{\cdot}NH_2)_2$, is obtained by cautiously reducing the corresponding dinitro-base with stannous chloride and hydrochloric acid at 0°, and treating the resulting *stannochloride* with ammonium sulphide; it forms colourless crystals, and melts at 187°. *Orthodiamidodibenzylparatoluidine* crystallises in small, colourless needles, and melts at 145°; the *hydrochloride* crystallises with 3 mols. H_2O, and the *sulphate* with 4 mols. H_2O. A. R. L.

Propylamidophenol and its Acetyl Derivatives. By P. Cazeneuve (*Compt. rend.*, **115**, 1312—1315).—When the propylamidophenol obtained from camphor (this vol., i, 152) is simply mixed with excess of acetic anhydride, there is a distinct and immediate rise of temperature, and if the product is precipitated with water and recrystallised from alcohol of 93°, the compound $OH{\cdot}C_9H_{10}{\cdot}NHAc$ is obtained in colourless prisms, which melt at 95—96° and are insoluble in water, but very soluble in chloroform, alcohol, and ether. It is insoluble in all acids, but dissolves in alkalis; an alcoholic solution gives an apple-green coloration with ferric chloride.

If the propylamidophenol is boiled with excess of acetic anhydride for 15 minutes, even without any sodium acetate, the *triacetyl* derivative, $OAc{\cdot}C_9H_{10}{\cdot}NAc_2$, is obtained, and, when recrystallised from alcohol, forms white, very light, slender needles. It melts at 138—139° to a colourless liquid, which readily remains in superfusion; at 200—250° under ordinary pressure, it distils with slight decomposition and liberation of acetic acid. It is insoluble in water, ether, benzene, and carbon bisulphide, and also in acids and alkalis, but dissolves readily in alcohol or chloroform. When boiled with water containing hydrochloric or sulphuric acid, it remains unaltered, but when boiled with a solution of an alkali hydroxide, it dissolves with hydrolysis, and afterwards undergoes further decomposition, the liquid becoming first yellow and then red.

Propylamidophenol in alkaline solution is an energetic developer of photographic plates, and hence, if Lumière's laws are correct (*Bull. Soc. Chim.*, 1892), the hydroxyl and amido-groups must be in the ortho- or para-position, and not in the meta-position, as assumed in a previous paper (*loc. cit.*). The para-position is improbable, but the ortho-position agrees well with the properties of the compound. Further researches have shown also that the compound from which the propylamidophenol is formed is a nitrophenol, and not a nitroketone as originally supposed. C. H. B.

Alkyl Orthodiamines. By F. Kehrmann and J. Messinger (*J. pr. Chem.* [2], **46**, 565—574; compare Abstr., 1892, 1472).—Orthonitrobenzylaniline melts at 74—75°, and orthonitromethylaniline at 34°.

New bases have been obtained by the oxidation of methyl- and ethylorthophenylenediamine by ferric chloride; the analysis of the hydrochloride of the methyl derivative corresponds with the formula $C_4H_{16}N_3OCl + H_2O$. Treatment of orthamidodiphenylamine with ferric chloride, yields a base, $C_{24}H_{19}N_3O$, which crystallises in brownish-red laminæ, having a bluish lustre, melts at 189—190°, and is soluble in most solvents, except water and cold alcohol. The constitution of these bases is not settled, but the probabilities are here discussed.

Dinitrophenylphenylorthophenylenediamine

$$[NHPh : NH{\cdot}C_6H_3(NO_2)_2 = 1 : 2],$$

prepared from dinitrobromobenzene and orthamidodiphenylamine heated together with sodium acetate, forms red, prismatic crystals,

melts at 170—171°, and is nearly insoluble in water, alcohol, and ether.

Paracetamidorthonitrodiphenylamine, $NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot COMe$, from paramidoacetanilide, sodium acetate, and orthonitrobromobenzene, crystallises in reddish-yellow laminæ, and melts at 147—148°.

Paranitrorthamidomethylaniline [$NHMe : NH_2 : NO_2 = 1 : 2 : 4$], obtained by reducing orthoparadinitromethylaniline, crystallises in dark red prisms, and melts at 177—178°. When a dilute hydrochloric acid solution of the base is mixed with pyrotartaric acid, a yellow, crystalline precipitate of methylketomethylnitrodihydroquinoxaline, $NO_2 \cdot C_6H_4 < \begin{matrix} N = CMe \\ NMe \cdot CO \end{matrix}$, is obtained; it has an intensely bitter taste. A. G. B.

Dibenzoyldiamidoethylene. By E. Bamberger and B. Berlé (*Ber.*, **25**, 3653—3654).—The authors have previously shown (Abstr., 1892, 632) that dibenzoyldiamidoethylene is formed by the action of benzoic chloride and soda on glyoxaline; on treating the amido-derivative with glacial acetic acid, it is converted into a second compound, having the same percentage composition and molecular weight as the dibenzoyldiamidoethylene, but differing from it in many of its chemical and physical properties; neither of these compounds is acted on by alcoholic potash, and their relationship is probably similar to that of maleïc and fumaric acids. J. B. T.

Diazobenzene. By A. Wohl (*Ber.*, **25**, 3631—3634).—A *benzoyl derivative* of diazobenzene, of the formula $NO \cdot NPh \cdot COPh$, is obtained on agitating a freshly prepared solution of potassium diazobenzene with excess of benzoic chloride. It crystallises in pale yellow needles, melts at 67° with explosive decomposition, and decomposes with evolution of gas when warmed in solution. It yields benzanilide when exposed to the air for 2—3 days, or when reduced with zinc-dust and acetic acid or ammonium sulphide. When treated with phenylhydrazine, it is converted into benzanilide and nitrous acid.

Silver diazobenzene, PhN_2OAg, is obtained by adding silver nitrate to a dilute alkaline solution of diazobenzene. It is a greyish-white powder, explodes very easily when dry, even when rubbed with a spatula, and decomposes in a capillary tube at 118°. When warmed with dilute nitric acid, it dissolves with a deep yellow coloration and the odour of nitrophenol. When heated with water above 65°, it is decomposed. This salt, therefore, differs from the stable silver diazobenzene prepared by Griess (*Annalen*, **137**, 54).

The alkaline solution of the silver salt, when treated with excess of ethyl iodide, yields a yellow oil containing nitrogen; it is not explosive, and is easily volatile with steam. E. C. R.

Azo- and Hydrazo-benzyl Alcohols. By C. Neubert (*J. pr. Chem.* [2], **46**, 580—581).—A *compound*, $C_{14}H_8N_2O_2$, is obtained by heating orthohydrazobenzoic acid (m. p. 205°) with acetic anhydride (in mol. prop.) and subliming the product; it crystallises in greenish-

yellow needles, and melts at 293°. The following have been prepared and will shortly be further described:—*Orthazobenzyl alcohol*, $N_2(C_6H_4\cdot CH_2\cdot OH)_2$, red laminæ, m. p. 165°. *Orthohydrazobenzyl alcohol*, $N_2H_2(C_6H_4\cdot CH_2\cdot OH)_2$, yellow laminæ, m. p. 123—124°. *Parahydrazobenzyl alcohol*, white flocculi, m. p. 196°. *Parazobenzyl alcohol*, dark red needles, m. p. above 300°. A. G. B.

Intramolecular Formation of the Azo-group. By E. Lellmann and N. Mayer (*Ber.*, **25**, 3578—3580; compare Abstr., 1892, 890).—*Orthazodibenzylaniline*, $NPh<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$, is obtained by heating on the water bath a saturated solution of orthodinitrodibenzylaniline in toluene with an excess of an alkaline solution of stannous chloride and an equal volume of alcohol; it crystallises in red needles, melts at 226°, and is sparingly soluble in cold benzene. *Orthazodibenzylparatoluidine*, $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot C_6H_4\cdot N\\ \|\\ CH_2\cdot C_6H_4\cdot N\end{matrix}$, is prepared in a manner similar to the aniline compound, which it resembles, and melts at 211°. When but a slight excess of stannous chloride is used in the last experiment, a red, amorphous *azoxy*-derivative,

$$O<\begin{matrix}N\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4Me)\cdot CH_2\cdot C_6H_4\cdot N\\ \|\\ N\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4Me)\cdot CH_2\cdot C_6H_4\cdot N\end{matrix}>O,$$

may also be isolated. Experiments which are now in progress show that nitro-compounds of the type $RN(CH_2\cdot C_6H_4\cdot NO_2)_2$, where R is an alkyl-group, give rise to the corresponding amido-derivatives on reduction in alkaline solution. A. R. L.

Diazoamido-compounds. By S. Niementowski (*Ber.*, **26**, 49—55).—It is usually supposed that the action of 1 mol. of nitrous acid on 1 mol. of an amido-compound always brings about the formation of the diazo-compound alone, but the author has observed cases in which a large quantity of the diazoamido-compound is formed under these conditions. So far as his experiments have gone at present, it appears that amido-compounds having neutral or only slightly acid properties yield considerable quantities of diazoamido-derivatives, whilst the strongly basic amido-compounds and those containing an acid group such as carboxyl yield solely the diazo-compounds. In the present paper, the results obtained in the treatment of orthamidoparatoluonitrile are discussed.

The preparation of diazoamidoparatoluonitrile has been described in a previous paper (*Monatsh.*, **10**, 591); the author has now investigated the yield given under different conditions, and finds that when 1 mol. of nitrous acid is used for 2 mols. of the amido-compound, a quantitative yield of the diazoamido-derivative is obtained as usual; moreover, if they are mixed in molecular proportion, the yield still amounts to 60 per cent., but it is decreased by the addition of excess of acid, until with a very large proportion of the latter the diazo-derivative is the sole product. Diazoamidotoluonitrile is converted by boiling alkali into metahomanthranilic acid, $NH_2\cdot C_6H_3Me\cdot COOH$,

and resinous products, probably formed from the metahomosalicylic acid, which is one of the primary products of the hydrolysis.

The metahomanthranilic acid, when diazotised under the conditions which give a yield of 60 per cent. of the diazoamido-derivative with amidotoluonitrile, forms solely the diazo-compound, probably owing to the presence of the strongly acid carboxyl-group.

Diazoamidoparatoluonitrile is acted on by α- and β-naphthol and by resorcinol with formation of azo-derivatives of paratoluonitrile, a more or less complete hydrolysis taking place simultaneously, so that azo-compounds of the corresponding metahomanthranilic acid are also obtained. These may also be directly obtained by the action of the phenols on the diazo-compound of the acid. *β-Naphtholazoparatoluonitrile*, $CN\cdot C_6H_3Me\cdot N_2\cdot C_{10}H_6\cdot OH$, forms long, blood-red, lustrous needles, melts at 272°, and dissolves in concentrated sulphuric acid with a cherry-red colour. The corresponding *β-naphtholazoparatoluic acid*, $COOH\cdot C_6H_3Me\cdot N_2\cdot C_{10}H_6\cdot OH$, crystallises in long, pale-red needles, and melts at 283°; *α-naphtholazoparatoluic acid* crystallises from acetic acid in slender matted needles, and melts at 270° with decomposition. Resorcinol yields with diazoamidoparatoluonitrile chiefly *resorcinoldisazoparatoluonitrile*, $C_6H_2(OH)_2(N_2\cdot C_6H_3Me\cdot CN)_2$, which is a brick-red, amorphous compound, and melts with decomposition at 287°.

H. G. C.

Conversion of Amines into Diazoimides by means of Azoimide. By E. Noelting and O. Michel (*Ber.*, **26**, 86—87).—Diazoimides are formed on adding a solution of sodium nitride or hydrogen nitride to a solution of a diazo-compound containing an excess of sulphuric acid. In this way, the authors have prepared diazoimides from aniline, ortho-, meta-, and para-nitranilines, 1, 2, 4-dinitraniline, and sulphanilic acid.

1, 2, 4-Dinitrodiazobenzeneimide, as obtained by this method, crystallises from dilute alcohol in white needles, and melts at 65° with decomposition.

E. C. R.

Action of Diazo-compounds on Hydrazines. By E. Noelting and O. Michel (*Ber.*, **26**, 88—92).—According to Fischer (*Ber.*, **10**, 1334), diazobenzeneimide and aniline are formed by mixing a solution of a phenylhydrazine salt with one of a diazobenzene salt. Griess (*Ber.*, **9**, 1659) obtained diazobenzeneimide, diazobenzeneimidecarboxylic acid, aniline, and amidobenzoic acid both by the action of diazometamidobenzoic acid on phenylhydrazine, and also by the action of diazobenzene on metahydrazinebenzoic acid. He also found that by the action of diazosuphanilic acid and diazonaphthionic acid on phenylhydrazine and of diazobenzene on parahydrazinebenzenesulphonic acid, both the diazo-compound and the hydrazine are converted into azoimides (*Ber.*, **20**, 1528).

When a solution of diazobenzene sulphate containing sufficient sodium acetate to neutralise the free mineral acid is added to an ice-cold solution of hydrazine sulphate, diazobenzeneimide, and ammonium sulphate are formed together with a small quantity of a compound which crystallises from alcohol in white needles. Neither

aniline nor hydrogen nitride could be detected in the products of the reaction.

Ortho-, meta-, and para-nitrodiazobenzene sulphates and hydrazine in the same way give theoretical yields of the diazoimide and ammonium sulphate. In no case was nitraniline and hydrogen nitride detected in the product.

1:2:4-Dinitrodiazobenzene sulphate in the same way yields dinitrodiazobenzeneimide, in a crystalline condition, and ammonia.

Diazosulphanilic acid and hydrazine yield ammonia and diazobenzeneimidesulphonic acid. The latter is isolated by means of its phenylhydrazine salt. E. C. R.

Action of Phenylcarbimide on Benzylbenzaldoxime. By E. BECKMANN and E. FELLRATH (*Annalen*, **273**, 1—30).—Beckmann (Abstr., 1891, 193) has stated that the compound melting at 122°, prepared by Goldschmidt (Abstr., 1890, 1412; 1891, 1477) and by Beckmann (*loc. cit.*), by treating β-benzylbenzaldoxime with phenylcarbimide, is decomposed by sodium ethoxide, yielding carbonic anhydride and a phenylimido-base of the composition $C_{20}H_{16}N_2$, which melts at 100°. The objects of this work were to try and ascertain the constitution of this base, and to obtain further information with regard to the action of phenylcarbimide in general. Although the former of these objects has been accomplished, the mechanism of the reaction by which the phenylimido-base is formed from β-benzylbenzaldoxime still requires elucidation.

The phenylimido-base is produced, but only in very small quantities, when β-benzylbenzaldoxime is treated with phenylthiocarbimide.

The phenylimido-base combines with methyl iodide at the ordinary temperature, yielding a substance which forms large, monoclinic crystals and which contains iodine; when this iodo-compound is treated with potash, it gives a *base* which crystallises in well-defined, monoclinic crystals, melts at 90·5°, and seems, from analyses and molecular weight determinations, to have the molecular formula $C_{21}H_{20}N_2$.

As it seemed probable, considering its origin and method of formation, that the base melting at 90·5° had the constitution

$$CH_2Ph{\cdot}NMe{\cdot}CPh{:}NPh,$$

its synthesis from benzylmethylamine, $CH_2Ph{\cdot}NHMe$, and benzanilidimidochloride, $CPhCl{:}NPh$, was attempted. When these two substances are heated together at 100°, they combine to form a crystalline *hydrochloride*, which, on treatment with potash, gives a crystalline *base* of the molecular formula $C_{21}H_{20}N_2$; this base forms well-defined crystals, melts at 67°, and is evidently not identical with the base melting at 90·5°. Nevertheless, a phenylimido-base melting at 100°, and identical with the compound obtained from the product of the action of phenylcarbimide on β-benzylbenzaldoxime, can be directly prepared by treating benzanilidimidochloride with benzylamine; this fact shows that in the phenylimido-base the carbon and nitrogen atoms are combined in the order given in the amidine

formula, $CH_2Ph{\cdot}NH{\cdot}CPh{:}NPh$, but it does not exclude as impossible the tetrahydroquinazoline constitution represented by the formula

$$C_6H_4<\begin{matrix}CH_2{\cdot}NH\\ |\\ NPh{\cdot}CHPh\end{matrix}.$$

In order to settle the question of the constitution of the phenylimido-base, the products of the interaction of benzanilidimidochloride and other amido-compounds were studied. A *base* of the molecular formula $C_{20}H_{18}N_2$ is obtained when benzanilidimidochloride is treated with orthotoluidine, and the hydrochloride produced in this way decomposed with potash; it crystallises in small, colourless needles, and melts at 110°. If reduced with sodium amalgam in boiling alcoholic solution, it yields a mixture of bases, which, when shaken with potash and benzenesulphonic chloride, gives orthotoluidinephenylsulphone, $C_6H_4Me{\cdot}NH{\cdot}SO_2Ph$ (m. p. 124°), and *benzylanilinephenylsulphone*, $CH_2Ph{\cdot}NPh{\cdot}SO_2Ph$. The last-named compound crystallises from alcohol in long needles, melts at 119°, and is easily separated from the other sulphone, as it is insoluble in potash. The readiness with which reduction takes place and the nature of the compounds so formed show that the original base, melting at 110°, is an *orthotolylphenylbenzenylamidine* of the constitution

$$C_6H_4Me{\cdot}NH{\cdot}CPh{:}NPh,$$

and not a tetrahydroquinazoline of the constitution

$$C_6H_4<\begin{matrix}CH_2{\cdot}NPh\\ |\\ NH{\cdot}CHPh\end{matrix}.$$

The *base* of the molecular formula $C_{26}H_{22}N_2$, prepared from benzanilidimidochloride and benzylaniline in like manner, melts at 111°; on reduction with sodium amalgam, it yields benzylaniline, so that it is doubtless a *phenylbenzylphenylbenzenylamidine* of the constitution $CH_2Ph{\cdot}NPh{\cdot}CPh{:}NPh$.

The results of the experiments just described having indicated a method by which the constitution of the phenylimido-base could be determined, the compound in question was reduced with sodium amalgam and the products separated with the aid of soda and benzenesulphonic chloride; in this way, *benzylaminephenylsulphone*, $CH_2Ph{\cdot}NH{\cdot}SO_2Ph$, melting at 87°, benzylanilinephenylsulphone, melting at 119°, and small quantities of anilinephenylsulphone, melting at 109°, were obtained, so that the phenylimido-base is doubtless a *benzylphenylbenzenylamidine* of the constitution given above; this view is confirmed by the fact that, as a secondary base, it interacts with benzenesulphonic chloride, yielding a compound melting at 148°, and also with benzyl chloride, forming an oily benzyl derivative.

When the base melting at 67°, obtained by the action of benzylmethylamine on benzanilidimidochloride, is reduced with sodium amalgam, it is decomposed into aniline, benzylaniline, and benzylmethylamine, which can be separated with the aid of benzenesulphonic chloride; *benzylmethylaminephenylsulphone*, $CH_2Ph{\cdot}NMe{\cdot}SO_2Ph$, crystallises from a mixture of ether and light petroleum in well-defined plates melting at 93°. When the base melting at 67° is

heated with hydrochloric acid at about 200°, it is decomposed into aniline, benzylmethylamine, and benzoic acid. These reactions show that the base is a *benzylmethylphenylbenzenylamidine* of the constitution represented by the formula $CH_2Ph{\cdot}NMe{\cdot}CPh{:}NPh$.

The base melting at 90·5°, prepared by methylating the phenylimido-base, is reduced by sodium amalgam in alcoholic solution, yielding dibenzylamine and methylaniline, which can be separated with the aid of benzenesulphonic chloride; *dibenzylaminephenylsulphone*, $SO_2Ph{\cdot}N(CH_2Ph)_2$, and *methylanilinephenylsulphone*,

$$NMePh{\cdot}SO_2Ph,$$

are crystalline compounds melting at 68° and 79° respectively. The base melting at 90·5° is also decomposed by concentrated hydrochloric acid at 200°, yielding methylaniline, benzylaniline, and benzoic acid. When treated with bromine in chloroform solution, the base is converted into a colourless compound of the composition $C_{21}H_{20}N_2Br_2$, which melts at 228—229° with decomposition; this bromo-derivative is readily decomposed by cold alcoholic silver nitrate, yielding a compound of the composition $C_{21}H_{19}N_2Br$, which crystallises in plates and melts at 102°. These reactions show that the base is a *phenylmethylbenzylbenzenylamidine* of the constitution represented by the formula $CH_2Ph{\cdot}N{:}CPh{\cdot}NMePh$.

Attempts to prepare the compound (benzylphenylcarbamide) melting at 168°, which, according to Goldschmidt (*Ber.*, **23**, 2746), is produced by the action of phenylcarbimide on β-benzylbenzaldoxime were unsuccessful. F. S. K.

Action of Amines and Ammonia on the Dinitrosacyls. By A. F. Holleman (*Rec. trav. Chim.*, **11**, 258—274; compare Abstr., 1889, 50; 1892, 971).—*Diphenyldinitrosacyl*, $\begin{matrix}CBz{:}N{\cdot}O\\ |\quad\ |\\ CBz{:}N{\cdot}O\end{matrix}$, is prepared by treating acetophenone with red nitric acid for 24 hours at the ordinary temperature. The product is washed with water and recrystallised from ether and glacial acetic acid, and amounts to 75 per cent. of the acetophenone used. It forms colourless, monoclinic tablets, of which full crystallographic details are given:—$a : b : c = 1·6156 : 1 : 1·6021$; $\beta = 61° 41'$. When diphenyldinitrosacyl is heated at 100° with dry aniline in ethereal solution, it is decomposed into benzanilide and a dark-brown, crystalline substance, which, on further cautious heating, is converted into a yellow, crystalline substance melting at 205°, and having the composition $C_{15}H_{11}N_3O_2$. This is much more stable than the dinitrosacyl, as it resists the action of concentrated hydrochloric acid at 110°; on boiling with strong potash, however, it is decomposed into ammonia, aniline, and benzoic acid. It is probably formed by the condensation of a second aniline molecule with the residue, $\begin{matrix}CBz{:}N{\cdot}O\\ |\quad\ |\\ CH{:}N{\cdot}O\end{matrix}$, left after the removal as benzanilide of one of the benzoyl groups of the dinitrosacyl, and has therefore, the constitution, $\begin{matrix}CBz{:}N{\cdot}NPh\\ |\quad\ |\\ CH{:}N{\cdot}O\end{matrix}$. By the further action of

aniline the second benzoyl group is also detached as benzanilide, whilst at the same time diphenylcarbamide is formed. The latter also results directly by boiling an aniline solution of the dinitrosacyl for some time. This formation of diphenylcarbamide bears a certain analogy to that of phenylcarbamide and diphenylguanidine by the action of aniline on mercuric fulminate, and suggests that the nucleus $C_2N_2O_2$ is the same in both fulminate and dinitrosacyl (compare Abstr., 1892, 64, 446), a view which is confirmed by the formation of a small quantity of guanidine along with benzamide, when diphenyldinitrosacyl is heated with 20 per cent. aqueous ammonia for three hours at 120—140°.

When paratoluidine is substituted for the aniline, the action is analogous, the product forming brilliant needles, melting at 210°, and having the composition $C_{16}H_{13}N_3O_2$. With alcoholic ammonia at 100°, a red product is formed, which on purification yields a substance crystallising in long, brillant, white needles, melting at 135°, and having the composition $C_9H_7N_3O_2$. It is completely broken up by prolonged heating with aqueous ammonia.

Dianisyldinitrosacyl behaves in a similar way with aniline, anisanilide and a white, crystalline substance melting at 125°, and having the composition $C_{16}H_{13}N_3O_3$, being formed.

Methylaniline has no action on the dinitrosacyls. Jn. W.

Phenylanilcyanamide and β-Diphenylsemithiocarbazide. By D. Tivoli (*Gazzetta*, **22**, ii, 379—386; compare Abstr., 1892, 1323).—On passing cyanogen chloride into an ethereal solution of diphenylhydrazine, the hydrochloride of the base separates and *phenylanilcyanamide*, $NPh_2{\cdot}NH{\cdot}CN$, remains in solution; this forms colourless crystals melting at 97°, and when pure is unaltered on exposure to the air. It is very soluble in alcohol or benzene, less so in acetic acid, and insoluble in water; it is decomposed by acids, and, with dilute potash, gives an intense blue liquid. It gives the normal molecular weight by the cryoscopic method in acetic acid solution. The *hydrochloride*, $NPh_2{\cdot}NH{\cdot}CN,2HCl$, forms minute, white needles melting at 162°; it is very soluble in alcohol, sparingly so in light petroleum, chloroform, or benzene, and insoluble in ether. It does not reduce Fehling's solution, but reduces ammoniacal silver nitrate, and with dilute copper sulphate solution, gives a magnificent red coloration, soon changing to violet. It reduces platinic and auric chlorides without combining with the salts. Its aqueous solution soon decomposes with separation of the base, which is best prepared in the pure state by this means. The *picrate*,

$$NPh_2{\cdot}NH{\cdot}CN,C_6H_3O(NO_2)_3,$$

is obtained in large, garnet-coloured crystals, which melt at 172° with decomposition; it is very soluble in benzene, and sparingly so in alcohol, ether, and water. On rapid heating, it decomposes explosively with carbonisation.

β-Diphenylsemithiocarbazide, $NH_2{\cdot}CS{\cdot}NH{\cdot}NPh_2$, is obtained by the action of ammonium sulphide on phenylanilcyanamide in alcoholic solution. It forms beautiful, colourless crystals, melts at 202°, and

gives a normal molecular weight by the cryoscopic method in acetic acid solution. It has a bitter taste, is very soluble in alcohol, benzene, chloroform, acetic acid, or acetone, sparingly so in ether, and insoluble in water or light petroleum. W. J. P.

Stereochemistry of Unsymmetrical Hydrazones. By A. HANTZSCH (*Ber.*, **26**, 9—17; compare Abstr., 1892, 338, 798, and following abstract).—The existence of stereochemically isomeric hydrazones of unsymmetrical ketones, X·CO·Y, has been proved in the case of the phenylhydrazone of anisyl phenyl ketone, and the diphenylhydrazones (unsymmetrical) of anisyl phenyl and paratolyl phenyl ketones. In these and other cases, only one, the α-, hydrazone is obtained by the action of the hydrazine on the ketone itself, but if, instead of the ketone, its chloride, X·CCl_2·Y, be used, then, in each of the cases above mentioned, two isomeric crystalline hydrazones are obtained. (In other cases an oil was obtained which could not be induced to crystallise, and was probably a mixture of the two isomerides.) The two substances are structurally identical, for they have the same composition, the same molecular weight as determined by Raoult's method, and are both decomposed by alcoholic hydrochloric acid into ketone and hydrazine. That they are isomeric, however, is evident from their difference in melting point, solubility, and chemical behaviour. But the isomerism is geometrical and not structural, for were it the latter, then a symmetrical ketone, X·CO·X, such as benzophenone, ought equally to yield two hydrazones, but this is not the case; further, the two possible structurally isomeric formulæ

$$\frac{X}{Y}\!>\!C{:}N\cdot NHPh \text{ and } \frac{X}{Y}\!>\!C\!<\!\begin{matrix}NH\\|\\NPh\end{matrix}$$

repesent the isomerism as conditioned by the presence of a "mobile hydrogen atom." But it cannot be thus conditioned, for the diphenylhydrazones also exhibit isomerism of this kind, although in them the "mobile hydrogen atom" is absent, being replaced by phenyl. It is therefore necessary to have recourse to geometrical formulæ for an explanation. The following formulæ are proposed, and, in assigning the second to the less stable β-hydrazone, the analogy with the isomeric oximes was used as a guide; in the case of these compounds, it is the less stable configuration which has the OH of the oximido-group nearer to the substituted phenyl.

$$\begin{matrix}C_6H_5\cdot C\cdot C_6H_4X\\ \|\\ R\cdot NPh\cdot N\end{matrix} \qquad \begin{matrix}C_6H_5\cdot C\cdot C_6H_4X\\ \|\\ N\cdot NPh\cdot R\end{matrix}$$

α-Hydrazone. β-Hydrazone.

The α-isomerides are more stable, more soluble, and have a higher melting point, than the β-compounds. The latter are almost entirely converted into the former by the action of hydrogen chloride, and by the successive action of acetic chloride and ammonia; by the latter method, however, a conversion of the α- into the β-variety can also be effected, but only to a very slight extent.

The paper also contains an attemped refutation of Auwers and V. Meyer's stereochemical formulæ for isomeric hydrazones, and, as an appendix, a reply by Meyer to these objections. C. F. B.

Stereochemical Phenylhydrazones and Diphenylhydrazones. By B. Overton (*Ber.*, **26**, 18—34).—This paper contains the experimental matter on which the deductions in the preceding abstract are based. The stereochemically isomeric hydrazones were obtained by mixing the ketochloride with the hydrazine in ethereal, or sometimes in acetic acid solution, great care being taken that all the materials were quite pure. When the reaction was complete, often only after several days, the phenylhydrazine chloride was filtered off, any excess of phenylhydrazine removed by shaking with hydrochloric acid, and the ethereal solution allowed to evaporate at the ordinary temperature. The α-hydrazone crystallises first, and then the β-; the yield of the latter was never greater than about 10 per cent. By the action of the hydrazine on the ketone, the α-variety only was obtained.

Anisyl phenyl ketochloride yields, with phenylhydrazine, an α-hydrazone, forming colourless, ill-defined crystals melting at 132°, and a β-hydrazone, which forms a pale-coloured powder, or small, transparent, crystalline scales, and melts at 90°; both of these dissolve in acetic chloride, yielding an additive compound,

$$OMe\cdot C_6H_4\cdot CPh{:}N\cdot NHPh,AcCl,$$

which forms a transparent, horny mass, decomposed by water into ketone and acetylphenylhydrazine, by ammonia into the hydrazone and acetamide. With benzoic chloride, an analogous reaction occurs. With diphenylhydrazine, the ketochloride yields an α-diphenylhydrazone crystallising in yellow prisms, and melting at 151—152°, and a somewhat darker β-compound melting at 115°. These are much more stable than the monophenyl compounds, and no cases of inter-conversion were observed.

Paratolyl phenyl ketone yields, with phenylhydrazine, the α-hydrazone in fine, white crystals melting at 109°. If the ketochloride is used, an oily product is obtained, from which no crystalline substance could be separated. With diphenylhydrazine, two diphenylhydrazones were obtained: the α- in yellow crystals melting at 122°, the β- in tiny, yellow crystals melting at 95—96°.

Parachlorobenzophonone yields a white phenylhydrazone melting at 106°, and a yellow diphenylhydrazone melting at 130°. From the ketochloride, uncrystallisable substances only were obtained.

Orthochlorobenzophenone yields only an oily monophenylhydrazone, and the same is the case with the ketochloride.

Chlorobenzile, $CPh\cdot O\cdot CPhCl_2$, yields, with phenylhydrazine, the dihydrazone in yellow crystals melting at 225°. With diphenylhydrazone, it, as well as benzile itself, yields only a monohydrazone in yellow crystals melting at 108°.

For the more general properties of these hydrazones, especially the isomeric ones, reference must be made to the preceding abstract. The formulæ of the two classes of compounds are as below.

CXY:N·NHPh,	CXY:N·NPh$_2$.
Phenylhydrazones.	Diphenylhydrazones.

C. F. B.

Hexahydrobenzoic acid. By O. Aschan (*Ber.*, **25**, 3658—3661). The author considers that the differences observed by Markovnikoff (this vol., i, 93) between hexahydrobenzoic acid and "heptanaphthenic acid" are insufficient to prove their isomerism; hexahydrobenzoic acid in alkaline solution is scarcely acted on by potassium permanganate, even in 11½ hours, whilst Δ^2-tetrahydrobenzoic acid is immediately oxidised. Markovnikoff's acid probably contained a little Δ^1-tetrahydrobenzoic acid (m. p. 29°), which would account for the different result observed by him.

The reduction of benzoic acid by means of sodium amalgam proceeds slowly, unless pure mercury is employed.

Calcium hexahydrobenzoate is stated by Markovnikoff to crystallise with $5H_2O$, whilst the author's analyses indicated $4H_2O$; and fresh determinations confirm the previous results; the difference is probably due to the method of drying the salt and to the solvent employed for its purification. J. B. T.

Acids from Baku Petroleum. By O. Aschan (*Ber.*, **25**, 3661—3670).—A summary of the author's previous work on this subject (compare Abstr., 1891, 737, and 1892, 1452, 1481) and on hydrobenzoic acids. The lower naphthenecarboxylic acids are not hexamethylene derivatives, and do not belong to the same polymethylene series as the hydrocarbons. Zalozieckí's suggestion (Abstr., 1891, 999), that the carboxylic acids are "lactoalcohols,"

$$C_nH_{2n-1}\cdot CH<\begin{matrix}CH_2\\O\end{matrix}>CH\cdot OH,$$

is disproved by the fact that they are not acted on by hydrochloric acid, even when heated with it at 250°, and they have all the properties of acids.

Zalozieckí states that on oxidation with sulphuric acid and potassium dichromate, heptanaphthenecarboxylic acid yields fatty acids of high molecular weight; the author is unable to confirm this, as, under the conditions stated, he obtained acetic and succinic acids in some quantity, together with unchanged heptanaphthenecarboxylic acid and a trace of oxalic acid. J. B. T.

Orthonitrobenzylmetamidobenzoic acid. By C. Paal and E. Fritzweiler (*Ber.*, **25**, 3590—3607).—*Orthonitrobenzylmetamidobenzoic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot COOH$, is prepared by boiling an alcoholic solution of orthonitrobenzyl chloride and metanitrobenzoic acid in molecular proportion for 6—7 hours; the main portion separates on cooling. It forms yellow leaflets, melts at 170—171°, and is insoluble in water. The *potassium* salt crystallises from alcohol in yellow needles, and melts at 196°; its aqueous solution gives precipitates on the addition of barium and calcium chlorides or of salts of the heavy metals. The *ethyl* salt forms small, amber-coloured crys,

tals, and melts at 100°. The nitro-group in this acid could not be reduced to the amido-group by means of zinc-dust. The *formyl* derivative, $NO_2 \cdot C_7H_6 \cdot N(COH) \cdot C_6H_4 \cdot COOH$, crystallises in brownish, jagged prisms, and melts at 195°; whilst the *acetyl* derivative forms small, yellowish crystals, and melts at 239°. Both these derivatives yield indazylbenzoic acid (see below) on reduction with tin and hydrochloric acid, or with zinc-dust and acetic acid, together with a compound melting at 156—157°, but hydrogenised quinazoylbenzoic acids are not produced (compare Abstr., 1892, 81).

Metindazylbenzoic acid, $C_6H_4<\begin{matrix}N- \\ | \\ CH\end{matrix}>N \cdot C_6H_4 \cdot COOH$, is obtained by reducing an alcoholic solution of the nitrobenzylamidobenzoic acid with tin and hydrochloric acid. It crystallises in concentrically grouped, white needles, melts at 211°, and is sparingly soluble in alcohol, benzene, and hot mineral acids. The *hydrochloride* and the acid *sulphate* are dissociated by water; the latter melts at 146—148°. An aqueous solution of the *sodium* salt gives precipitates with barium and calcium chlorides, and with salts of the heavy metals. The *ethyl* salt melts at 92°.

Orthometazobenzenedicarboxylic acid, $N_2(C_6H_4 \cdot COOH)_2$, is formed by oxidising metindazylbenzoic acid, dissolved in glacial acetic acid, with chromic acid. It crystallises in aggregates of red needles, melts at 237° with decomposition, and is sparingly soluble in alcohol and ether. Aqueous solutions of the *alkali* salts do not give a precipitate with barium chloride until boiled with it. The *hydrazo-acid* is obtained by reducing an ammoniacal solution with zinc-dust; it crystallises in small, almost white needles, melts at 206° with decomposition, and is readily soluble in the ordinary solvents. A solution of the *sodium* salt gives no precipitate with barium chloride, but voluminous precipitates are produced with lead and zinc salts, as also with silver nitrate; the *silver* salt is very unstable. When the azo-acid is reduced with tin and hydrochloric acid, *orthometabenzidinedicarboxylic acid* is formed; it is being further examined. A. R. L.

Ethyl Azobenzenecyanacetate. By F. Krückeberg (*J. pr. Chem.* [2], **46**, 579—580; compare Haller, Abstr., 1888, 823).—This compound may be prepared by the action of diazobenzene chloride on ethyl cyanacetate in presence of sodium acetate; it crystallises in silky needles, and melts at 106—108°. The *potassium compound*, $C_{11}H_{10}KN_3O_2 + 2H_2O$, was obtained, and from this the other metallic compounds, which are mostly coloured and sparingly soluble, were prepared. When the solution of the potassium compound is treated with excess of acetic or hydrochloric acid, the original compound (m. p. 108°) is obtained; but if the calculated quantity of acid be employed, an *isomeride*, which crystallises in rhombohedra and melts at 82°, is isolated. The isomeride of higher melting point requires 40 times its weight of benzene to dissolve it at the ordinary temperature; the other only requires four times its weight. Warming with hydrochloric acid will also effect the conversion from the higher melting point to the lower; hot acetic anhydride effects the reverse change. The *ethyl* derivative, $N_2Ph \cdot CEt(CN) \cdot COOEt$, obtained from the

potassium compound and ethyl bromide, forms rhombic crystals, and melts at 72°; the *benzoyl* derivative crystallises in needles, and melts at 158°. A *dibromo-derivative*, $C_{11}H_9Br_2N_2O_3$, and the *amide*,

$$N_2Ph{\cdot}CH{\cdot}(CN){\cdot}CONH_2$$

(m. p. 245°), were prepared, the latter from both isomerides.

A. G. B.

Anilidosalicylic acid. By R. Dierbach (*Annalen*, **273**, 117—126).—*Anilidosalicylic acid*, $NHPh{\cdot}C_6H_3(OH){\cdot}COOH$

$$[OH : COOH : NHPh = 1 : 2 : 4],$$

is formed in small quantities, together with dianilidoquinoneanil, azophenine, and resinous products, when diazosalicylic acid is treated with aniline in benzene solution, a very energetic reaction taking place with evolution of nitrogen and carbonic anhydride. It crystallises in colourless needles, melts at 217·5°, is almost insoluble in cold water, and gives a violet coloration with ferric chloride; on distillation with lime, it seems to yield paranilidophenol. The *barium* salt, $(C_{13}H_{10}NO_3)_2Ba + 6H_2O$, is readily soluble in hot, but only sparingly in cold, water, and begins to decompose at 231°. The *sulphate*, $(C_{13}H_{11}NO_3)_2,H_2SO_4$, crystallises in rose-coloured tufts, and dissolves freely in water and alcohol.

Aniline bromosalicylate, $C_7H_5BrO_3,NH_2Ph$ [OH : Br : COOH = 1 : 2 : 4], crystallises from hot water in long needles, and melts at 134°.

Bromosalicylanilide, $OH{\cdot}C_6H_3Br{\cdot}CO{\cdot}NHPh$, is formed when aniline bromosalicylate is treated with phosphorus trichloride and the mixture heated at 170°; it crystallises from alcohol in long needles, melts at 222°, and is soluble in soda.

Dinitranilidosalicylic acid, $COOH{\cdot}C_6H_3(OH){\cdot}NH{\cdot}C_6H_3(NO_2)_2$

$$[OH : COOH : NH = 1 : 2 : 4],$$

can be obtained by heating an alcoholic solution of amidosalicylic acid with dinitrochlorobenzene at 130°; it crystallises in slender, red needles, melts at 272°, and dissolves in alkalis with a dark red coloration.

Diamidanilidosalicylic acid, $COOH{\cdot}C_6H_3(OH){\cdot}NH{\cdot}C_6H_3(NH_2)_2$, prepared by reducing the preceding compound with stannous chloride, is a colourless substance, but its solutions in alkalis quickly turn deep blue, and its acid solutions reddish. The *sulphate* crystallises in rose-coloured needles.

Nitramidanilidosalicylic acid, $COOH{\cdot}C_6H_3(OH){\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}NO_2$, is obtained when the dinitranilido-acid is reduced with ammonium sulphide; it forms red crystals, and is soluble in acids.

Nitrophenylazimidosalicylic acid,

$$NO_2{\cdot}C_6H_3{<}\begin{matrix}N\\|\\N\end{matrix}{>}N{\cdot}C_6H_3(OH){\cdot}COOH,$$

is formed when the preceding compound is treated with amyl nitrite and hydrochloric acid in alcoholic solution; it crystallises in colourless needles, and melts at 269° with decomposition. F. S. K.

The Stereoisomeric Isopropylphenylglycollic acids. By M. Fileti (*J. pr. Chem.* [2], **46**, 560—563).—These acids are separated by means of quinine and cinchonine. By recrystallising the quinine salts from aqueous alcohol, the lævorotatory acid is obtained pure, but the dextrorotatory acid cannot be freed from the lævorotatory. On the other hand, when the cinchonine salts are recrystallised, the dextrorotatory acid is obtained pure. Both acids crystallise in thick tables which melt at 153—154°, whereas the inactive mixture forms laminæ, and melts at 156—157°. 100 parts of absolute alcohol at 13° dissolve 47·49 parts of the dextrorotatory acid, 47·32 of the lævorotatory, and 21·61 of the inactive. For the dextro-acid, $[\alpha]_D = 134·9°$ ($c = 4·0568$, $l = 2$, $t = 17°$, $\alpha = 10·95°$); for the lævo-acid, $[\alpha]_D = -135°$ ($c = 4·0916$, $l = 2$, $t = 17°$, $\alpha = -11·05°$). Both acids lose their activity when heated with water in a sealed tube at 180—200° for 40 hours. The lævo-quinine salt crystallises in needles, and melts at 204—205°; the dextro-quinine salt forms slender needles, and melts at 192—193°; the dextro-cinchonine salt crystallises in long, lustrous needles, and melts at 201°; the lævo-cinchonine salt also forms needles, and melts at 167°; the solubility and rotation of these salts are given.

When either of these acids is treated with saturated hydrochloric acid, it is converted into inactive isopropylphenylchloracetic acid, which is immediately decomposed by water, and by treatment with soda, yields inactive isopropylphenylglycollic acid. A. G. B.

Derivatives of Homoterephthalic acid. By M. Fileti and E. Cairola (*J. pr. Chem.* [2], **46**, 563—564).—*Nitrohomoterephthalic acid* [$COOH : NO_2 : CH_2·COOH = 1 : 3 : 4$], the product of the nitration of homoterephthalic acid, crystallises in straw-coloured tables, melts at 222—223°, and dissolves in hot water and alcohol, but sparingly in the other ordinary solvents. The *methyl salt* is colourless, and melts at 75—77°; excess of ammonia imparts an amethyst colour to its alcoholic solution. When the acid is heated with alcoholic ammonia at 120°, it is split up into carbonic anhydride and metanitroparatoluic acid (m. p. 189°); treatment of the chloride of this acid with ammonia yields *metanitrotoluamide*, which crystallises in long, yellow needles, melts at 165—166°, and is sparingly soluble.

Oxindolecarboxylic acid, $COOH·C_6H_3<\begin{matrix}CH_2\\NH\end{matrix}>CO$, is the product of the reduction of nitrohomoterephthalic acid by ammonium sulphide; it forms yellow crystals, melts at 313°, and is sparingly soluble. Its *ammonium* salt, with 2 mols. H_2O, and *barium* salt, with $3\frac{1}{2}$ mols. H_2O, were prepared. A. G. B.

Chebulic acid. By W. Adolphi (*Arch. Pharm.*, **230**, 684—705).—This acid is obtained from myrobalans, the fruits of *Terminalia chebula*, best in the following manner:—The dried fruits are powdered, macerated for 10 days at the ordinary temperature with 90 per cent. alcohol, pressed, and filtered. The alcohol is completely removed from the extract, and the residue then dissolved in hot

water; cold water is added until no further milkiness appears, and the whole is allowed to settle, and then filtered. To the filtrate, sodium chloride is added until a permanent turbidity appears, and the solution is then shaken out with ethyl acetate, which dissolves chebulic and tannic acids. To remove the latter, the ethyl acetate is distilled off, and the residue dissolved in water, and shaken out with ether; from the aqueous solution, crystals of chebulic acid then separate on standing, and may be recrystallised from hot water. The yield is 3·5 per cent.

Chebulic acid, $C_{28}H_{24}O_{19} + H_2O$, begins to melt at about 200°, and is optically active, having $[\alpha]_D = +66{\cdot}94°$. The molecular weight of the anhydrous compound was determined by Beckmann's boiling-point method in acetone solution. The acid seems to be monobasic and forms an amorphous *barium salt*, $(C_{28}H_{23}O_{19})_2Ba$, which is white when moist, and green when dry, and a grey, amorphous, basic (?) *zinc salt*, probably $(C_{28}H_{23}O_{19})_2Zn + ZnO$. These salts appear, in general, to be decomposed by water, even in the cold. With strychnine, an acid salt, $C_{19}H_{22}N_2O,2C_{28}H_{24}O_{19}$, is formed. With benzoic chloride and soda, a yellowish, amorphous *benzoyl derivative*, $C_{28}H_{20}Bz_4O_{15}$, melting at 88·5°, is obtained. With phenylhydrazine, chebulic acid yields a derivative in the form of a reddish powder, which melts at 142°, and, when dissolved in alcohol and treated with strong aqueous potash, yields a momentarily green, then mulberry-red, and, finally, brownish-red coloration. (Tannic acid, similarly treated, gives a green colour, only gradually changing to red; gallic acid, an immediate red coloration.) When chebulic acid is dissolved in alcohol and the solution saturated with gaseous hydrogen chloride, some ethyl gallate is formed, and, in addition, a yellow, amorphous acid, somewhat analogous in its properties to tannic acid. Sulphuric acid hydrolyses chebulic acid to gallic acid and other undetermined products. C. F. B.

A Derivative of Amidoacetal. By W. Marckwald and A. Ellinger (*Ber.*, **26**, 98—100).—*Dibenzenesulphodihydroaldine*, $SO_2Ph{\cdot}N{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}NSO_2Ph$, is obtained by shaking benzenesulphoamidoacetal, $SO_2Ph{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$, with concentrated hydrochloric acid and then warming the mixture on the water-bath. It separates from hot alcohol in white crystals, melts at 163°, and is sparingly soluble. When reduced with sodium in boiling amyl alcohol, it is converted into diethylenediamine. E. C. R.

Acetylnitrocarbazole. By G. Mazzara and E. Leonardi (*Gazzetta*, **22**, ii, 443—444).—The nitrocarbazole melting at 209—210° (Abstr., 1891, 576) yields an *acetyl* derivative which crystallises in yellowish, thin needles melting at 237—238° (corr.); it is soluble in chloroform or toluene and sparingly so in alcohol or light petroleum. The same acetylnitrocarbazole (compare Abstr., 1892, 616) is obtained on nitrating acetylcarbazole in acetic acid solution. W. J. P.

Condensation of Ketones with Phenols. By A. Dianin (*J. Russ. Chem. Soc.*, **23**, 488—517, 523—546, 601—611).—Acetone (220 grams) was mixed with phenol (1600 grams) and glacial acetic acid (1800 grams), and to this mixture, fuming hydrochloric acid of sp. gr. 1·19 (600 c.c.) was added, the whole being heated in a stoppered vessel for 24 hours at 40—50°. On cooling, crystals separated, and, after these had been collected on an asbestos filter, the filtrate was again heated as before, the treatment being repeated until no more crystals were obtained from the filtrate on further heating. The total weight of the crystalline product was 750—800 grams on each occasion, from which 700 grams of the purified substance was obtained, after distilling off the phenol with steam, and recrystallising from hot 30 per cent. acetic acid. The crystals, on analysis, gave numbers corresponding with the formula $C_{15}H_{16}O_2$, and were proved to be *dimethyldiphenoxymethane*, $CMe_2(C_6H_4{\cdot}OH)_2$, formed by the condensation of acetone and phenol.

Dimethyldiphenoxymethane is soluble in 2820 parts of water at the ordinary temperature, and in 130 parts at the boiling point. It is easily soluble in alcohol, ether, acetic acid, and alkalis. From hot saturated aqueous solutions, it crystallises in feathery needles, and from dilute solutions in microscopic prisms, or sometimes in what appear to be quadratic plates. Its melting point is 151—152°, and, on boiling, it decomposes, giving off phenol. With ferric chloride, it gives a pale violet coloration, which disappears rapidly, and the green solution in concentrated sulphuric acid also changes to violet on the addition of ferric chloride. The *dibenzoyl* compound, $C_{15}H_{14}O_2Bz_2$, melts at 153—155°; it is not attacked by aqueous potash, but is decomposed by alcoholic potash. The *dimethyl ether*, $CMe_2(C_6H_4{\cdot}OMe)_2$, is prepared by boiling the diphenol (50 grams) with potash (30 grams) and methyl iodide (65 grams) in methyl alcohol solution for 10 hours with a reflux condenser. It crystallises in the rhombic system, is easily soluble in alcohol and ether, melts at 60·5°, and boils without decomposition at 371°.

Diethyldiphenoxymethane, $CEt_2(C_6H_4{\cdot}OH)_2$, was prepared by heating, in a sealed tube, diethyl ketone (63 grams), phenol (374 grams), and hydrochloric acid, sp. gr. 1·19 (70 grams), with continued shaking, for 24 hours at 80—90°. About 80 grams of crude crystalline product was obtained, and this, on repeated recrystallisation from 25 per cent. alcohol, gave needles melting at 198—200°. It is almost insoluble in water, but dissolves readily in ether, alcohol, and alkalis. Fusion with alkali, or heating at 100° with fuming hydrochloric acid, gives paramylphenol, $C_5H_{11}{\cdot}C_6H_4{\cdot}OH$. The *dibenzoyl* compound melts at 162·5°.

Dipropyldiphenoxymethane, $CPr_2(C_6H_4{\cdot}OH)_2$.—Butyrone (1 part) was heated for 30 hours at 60° with phenol (4 parts) and hydrochloric acid, sp. gr. 1·19 (1 part). 18 grams of butyrone gave 10 grams of crude product, which was purified by recrystallisation from dilute alcohol. It melts at 155°, crystallises in needles, and resembles the diethyl compound in its solubility relations. Fuming hydrochloric acid at 100° converts it into heptylphenol. The *dibenzoyl* compound melts at 144—145°.

Methylhexyldiphenoxymethane, $C_6H_{13}\cdot CMe(C_6H_4\cdot OH)_2$, was prepared from methyl hexyl ketone (20 grams), phenol (80 grams), and fuming hydrochloric acid (20 grams), by heating for 24 hours at 80—90°. The product was washed several times with warm water to remove phenol and hydrochloric acid, and afterwards distilled with steam, which removed the unattacked methyl hexyl ketone. The residue was then dissolved in benzene and precipitated by petroleum, when it came down as an oil, which crystallised in the course of a fortnight. The pure substance is soluble in alcohol, ether, benzene, glacial acetic acid, and alkalis. Water precipitates it from the acetic acid solution in the form of fine, silky needles melting at 83·5°. Heating with fuming hydrochloric acid for 36 hours at 100° gives octyl phenol. The dibenzoyl compound melts at 114°.

When phenol is oxidised in acid solution by means of potassium permanganate, the diphenol formed, $OH\cdot C_6H_4\cdot C_6H_4\cdot OH$, is a di-para-compound. Similarly, the compounds above described are also di-para-compounds, as was proved by the author, who found anisic acid amongst their products of oxidation by means of chromic acid.

With regard to the conditions of the reaction of phenols with ketones, the author finds that 50—60° is the most favourable temperature, as at 100° a considerable quantity of tarry matter is formed. A very small quantity of fuming hydrochloric acid can effect the condensation, and even dilute acid (4 per cent.) is not without action. Under the same conditions, the reaction goes more slowly, the greater the molecular weight of the ketone employed; the rate of decomposition of the product by heating with fuming hydrochloric acid proceeds in the inverse order. As to the mechanism of the reaction, the author is inclined to assume the following phases:—

I. $COMe_2 + HCl = CMe_2Cl\cdot OH$.
II. $CMe_2Cl\cdot OH + C_6H_5\cdot OH = CMe_2(O\cdot C_6H_5)\cdot OH + HCl$.
III. $CMe_2(O\cdot C_6H_5)\cdot OH + C_6H_5\cdot OH = CMe_2(O\cdot C_6H_5)_2 + H_2O$.

The substance $CMe_2(OC_6H_5)_2$ then undergoes an isomeric transformation into $CMe_2(C_6H_4\cdot OH)_2$.

The dialkyldiphenoxymethanes, when fused with potash or heated with fuming hydrochloric acid, are decomposed according to the equation $R_2C(C_6H_4\cdot OH)_2 + H_2O = R_2CH\cdot C_6H_4\cdot OH + C_6H_4(OH)_2$.

The dihydroxybenzene might be expected to be quinol, but a large quantity of tar and of amorphous coloured substances are always formed, probably as products of the interaction of the quinol with the original diphenol.

1:4-*Isopropylphenol*.—Fuming hydrochloric acid has no action on dimethyldiphenoxymethane, but fusion with potash yields 1:4-isopropylphenol, which melts at 61°, boils at 227—228°, and is identical with that prepared by Paternò and Spica.

1:4-*Amylphenol*, $CHEt_2\cdot C_6H_4\cdot OH$, may be prepared from the diethyldiphenol, either by fusion with potash or by the action of fuming hydrochloric acid. It is easily soluble in ether, alcohol, and acetic acid; from either of the latter it may be precipitated by the addition

of water in the form of fine, silky needles. It melts at 79·5—80°, and distils without decomposition at 253°. Ferric chloride gives no coloration. In strong alkaline solution, it only dissolves with difficulty, although it is easily soluble in weak alkalis. The benzoyl compound melts at 54—55°.

1 : 4-*Heptylphenol*, $CHPr_2{}^{\beta}\cdot C_6H_4\cdot OH$.—Butyrone (1 part), phenol (4 parts), and hydrochloric acid (sp. gr. 1·19, 3 parts) were heated for 48 hours at 100°. The product was washed with water and distilled over with steam; the oil thus obtained was treated with 2 per cent. potash solution, from which the dissolved phenol was liberated by a stream of carbonic anhydride, and again subjected to distillation with steam. Heptylphenol has a pleasant odour, is insoluble in water, and easily soluble in alcohol, ether, and acetic acid. It is volatile with steam, melts at 70—71°, and boils at 281°. The *benzoyl* compound melts at 29·5—30°, and the *methyl ether* distils at 267—268°, its sp. gr. at 0°/4° being 0·9349.

1 : 4-*Octylphenol*, $C_6H_{13}\cdot CHMe\cdot C_6H_4\cdot OH$, may be prepared, similarly to heptylphenol, from methyl hexyl ketone. It is a liquid having an unpleasant odour, and closely resembling in its properties the compounds above described. The benzoyl compound is also liquid.

The author found that α-naphthol condenses readily with acetone to give the compound *α-oxydinaphthylenedimethylmethane*,

$$CMe_2<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O.$$

Acetone (1 mol.) and α-naphthol (2 mols.) were dissolved in glacial acetic acid, and to the solution was added as much fuming hydrochloric acid as possible without occasioning the precipitation of the naphthol. The mixture was heated in a stoppered bottle at 80—100° until the contents solidified to a dense, crystalline mass. The crystals were pressed and recrystallised, first from alcohol and then from acetic acid. From ether, the substance crystallises in four-sided, almost quadratic, plates, which melt at 186°, and are always coloured slightly pink. J. W.

Condensation Products of Dimethylresorcinol and Methylresorcinol with the Nitrobenzaldehydes. By M. Zenoni (*Gazzetta*, **22**, ii, 298—303; compare Abstr., 1891, 620, *et seq.*).—*Metanitrophenylmetadimethoxyphenylmethane*, $NO_2\cdot C_6H_4\cdot CH(C_6H_3(OMe)_2)_2$, is obtained by heating dimethylresorcinol and metanitrobenzaldehyde with dilute sulphuric acid. It forms a yellow powder which begins to decompose at 158—160°, and does not melt; it is very soluble in ethyl acetate, less so in acetic acid, and only sparingly in benzene, light petroleum, and carbon bisulphide. The *para*-isomeride has very similar properties, but the *ortho*-compound is unstable.

Metanitrophenylmetahydroxymethoxyphenylmethane,

$$NO_2\cdot C_6H_4\cdot CH(C_6H_2(OH)\cdot OMe)_2,$$

is obtained as a yellow powder by heating metanitrobenzaldehyde and

methylresorcinol with dilute sulphuric acid. It resembles the substances described above, and begins to decompose at 150°.

W. J. P.

Xanthone Derivatives and Orthocresotic Anhydride. By M. Schöpff (*Ber.*, **25**, 3642—3647).—*4-Methylxanthone*,

$$C_6H_3Me<\begin{matrix}-O\\CO\end{matrix}>C_6H_4,$$

is obtained, together with dimethylxanthone, by the distillation of phenyl orthocresotate. It is more soluble in alcohol than dimethylxanthone, and is separated by precipitating the alcoholic mother liquors with dilute soda. It crystallises in colourless needles, melts at 105°, boils at 350—355°, and, with sulphuric acid, gives a yellow solution, which exhibits a bluish-green fluorescence.

4:5-*Dimethylxanthone* crystallises in colourless needles, and melts at 171—172°. It is more easily obtained by the distillation of orthocresyl orthocresotate, and comes over at 350—360°. It is obtained, together with orthocresotic anhydride, by heating orthocresotic acid and acetic anhydride in a reflux apparatus, and then distilling the product.

Orthocresotic anhydride, $(C_8H_8O_2)_2$, is a white, crystalline powder; it melts at 224—225°, is very sparingly soluble in most solvents, insoluble in alkaline carbonates, and when boiled with caustic alkalis, slowly dissolves, and is converted into orthocresotic acid.

4:5-*Xanthonedicarboxylic acid*, $COOH\cdot C_6H_3<\begin{matrix}CO\\-O\end{matrix}>C_6H_3\cdot COOH$, is obtained by oxidising dimethylxanthone with potassium permanganate. It crystallises in beautiful, white needles, does not melt at 285°, and dissolves in concentrated sulphuric acid with a yellow coloration and a pale, bluish-green fluorescence.

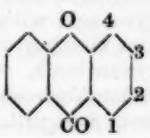
E. C. R.

Constitution of the Monhydroxyxanthones. By E. Dreher and S. v. Kostanecki (*Ber.*, **26**, 71—78; compare Abstr., 1892, 1096, 1097, 1099).—Graebe has shown that α-hydroxyxanthone is a true hydroxy-derivative of xanthone, since it yields methylenediphenylene oxide on distillation with zinc-dust; the authors find that when β-hydroxyxanthone is distilled with zinc-dust, it is converted into xanthene (m. p. 96°) which, on oxidation, yields xanthone; 4-hydroxyxanthone* shows the same behaviour.

1-*Hydroxy*-2:4-*dimethylxanthone*, $C_{13}H_5O_2Me_2\cdot OH$, is obtained, together with xanthone, when a mixture of metaxylo-orcinol,

$$[Me_2:(OH)_2 = 1:3:4:6],$$

salicylic acid, and acetic anhydride is distilled; it crystallises in long,

* The following system of numbering is adopted 

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yellow needles, melts at about 160°, and forms an intensely yellow sodium derivative which is insoluble in boiling water.

From its method of formation, this compound must have the constitution assigned to it, that is to say, the hydroxyl group is in the 1-position; the hydroxyl group in α-hydroxyxanthone and in α-hydroxymethylxanthone, both of which resemble hydroxydimethylxanthone very closely in properties, is therefore in the 1-position, whereas in β-hydroxyxanthone it is in the 3-position.

Orthodixanthone, $C_{26}H_{10}O_4$, is formed in the preparation of 4-hydroxyxanthone from salicylic acid and catechol (*loc. cit.*); it crystallises from glacial acetic acid in long, colourless needles, melts at 317°, and dissolves in concentrated sulphuric acid, yielding a yellow solution which shows a greenish fluorescence.

The properties of the four monhydroxyxanthones can be readily accounted for and brought into agreement with the above view of their constitution; the differences in colour which they exhibit are due to the difference in the position of the hydroxyl group relative to the chromophore CO.

Experiments on the behaviour of the hydroxyxanthones on treatment with methyl iodide and alcoholic potash have shown that 1-hydroxyxanthone cannot be converted into its methyl derivative, whilst the methyl derivatives of the other monhydroxyxanthones are easily obtained.

2-*Methoxyxanthone*, $C_{14}H_{10}O_3$, crystallises from alcohol in colourless needles, and melts at 131·5°; its solution in concentrated sulphuric acid shows a yellowish-green fluorescence.

3-*Methoxyxanthone* crystallises from alcohol in colourless needles, melts at 128·5°, and its solution in sulphuric acid shows a bluish fluorescence.

4-*Methoxyxanthone* forms colourless needles, and melts at 165°; it dissolves in sulphuric acid, yielding a yellow solution.

1-*Hydroxy*-3-*methoxyxanthone*, $OH\cdot C_{13}H_6O_2\cdot OMe$, is formed when isoeuxanthone is heated with methyl iodide and alcoholic potash; it crystallises from glacial acetic acid in needles, melts at 145°, and forms a sparingly soluble sodium derivative very similar to that of 1-hydroxyxanthone. F. S. K.

Preparation of Hydroxyxanthones from the Salols of Polyhydric Phenols. By W. Baumeister (*Ber.*, **26**, 79—82).—*Disalicylresorcinol*, $C_6H_4(O\cdot CO\cdot C_6H_4\cdot OH)_2$, can be obtained by heating resorcinol with salicylic acid; it crystallises in colourless needles, and melts at 111°; when heated for some hours, and then distilled, it yields 1-hydroxyxanthone, 3-hydroxyxanthone, xanthone, and a dixanthone melting at 256°, and identical with the compound described by Kostanecki and Seidmann (Abstr., 1892, 1097).

Disalicylquinol, $C_{20}H_{14}O_6$, prepared by heating a mixture of quinol and salicylic acid with phosphorus oxychloride, crystallises in colourless needles melting at 148°; on distillation, it yields xanthone and 2-hydroxyxanthone.

Dinaphthosalicylresorcinol, $C_6H_4(O\cdot CO\cdot C_{10}H_6\cdot OH)_2$, obtained in like manner from β-naphtholcarboxylic acid, crystallises in needles melting

at 232—233°; on distillation, it yields hydroxyphenonaphthoxanthone (compare Kostanecki, Abstr., 1892, 1099) and γ-dinaphthoxanthone.

F. S. K.

Condensations with Potassium Cyanide. By A. SMITH (*Ber.*, 26, 60—65; compare Chalanay and Knoevenagel, Abstr., 1892, 619).—Desylacetophenone is formed, together with a considerable quantity of a very sparingly soluble substance, when a solution of benzoïn and acetophenone in dilute alcohol is boiled with a small quantity of potassium cyanide; the sparingly soluble product combines directly with bromine, and seems to consist of a mixture of two or more, possibly isomeric, compounds.

A compound of the constitution

$$C_6H_4Pr\cdot CO\cdot CH(CH_2\cdot COPh)\cdot C_6H_4Pr,$$

which the author names *phenacyldesoxycuminoïn*, is formed, together with other substances, when cuminoïn is treated with acetophenone and potassium cyanide under the conditions mentioned above; it crystallises in colourless needles, and melts at 145°.

Phenacyldesoxypiperonoïn,

$$CH_2<^{O}_{O}>C_6H_3\cdot CO\cdot CH(CH_2\cdot COPh)\cdot C_6H_3<^{O}_{O}>CH_2,$$

obtained from piperonoïn and acetophenone in like manner, melts at 155°.

αβ-Dicumyl-α′-phenylfurfuran, $C_{28}H_{28}O$, is formed when phenacyldesoxycuminoïn is dissolved in concentrated sulphuric acid; it crystallises from dilute alcohol in colourless plates melting at 85°. The *hydrazone*, $C_{34}H_{34}N_2$, prepared by treating phenacyldesoxycuminoïn with phenylhydrazine in glacial acetic acid solution, crystallises in colourless needles, and melts at 162—163°; its constitution was not determined.

F. S K.

Condensation of Acetone with Benzoïn by means of Potassium Cyanide. By A. SMITH (*Ber.*, **26**, 65—71).—*Ketohydroxytriphenyltetrahydrobenzene*, $C_{24}H_{20}O_2$, is produced when a solution of benzoïn and acetone in dilute alcohol is heated with a small quantity of potassium cyanide; it crystallises from glacial acetic acid in long, colourless needles, melts at 248°, and is identical with the compound obtained by Japp and Raschen (Trans., 1890, 783), but to which they assigned the composition $C_{24}H_{28}O_3$. The *oxime*, $C_{24}H_{21}NO_2$, is obtained when the ketobenzene derivative is treated with hydroxylamine hydrochloride in alcoholic solution; it crystallises in colourless needles, and melts at 233—234°. The *hydrazone*, $C_{30}H_{26}N_2O$, crystallises in yellow needles melting at 197°.

Acetyltriphenylphenol, $C_6H_2Ph_3\cdot OAc$ [OAc : Ph_3 = 1 : 3 : 4 : 5], is formed when the ketobenzene derivative is boiled with acetic anhydride and a trace of zinc chloride; it crystallises in long, colourless needles, melts at 189°, and is converted into triphenylphenol on hydrolysis with alcoholic potash.

Triphenylphenol, $C_{24}H_{18}O$, separates from alcohol in thick needles, melts at 226°, and is insoluble in potash; on distillation with zinc-

dust, it yields a *triphenylbenzene* which melts at 157°, and has probably the constitution [$Ph_3 = 1:2:3$].

Ketohydroxytriphenyltetrahydrobenzene can also be obtained by the condensation of benzoïn with benzalacetone in presence of potassium cyanide; this fact, and the reactions described above, show that its constitution is probably represented by the formula

$$CO<\begin{matrix}CH=CPh\\ CH_2\cdot CHPh\end{matrix}>CPh\cdot OH;$$

it is also formed, together with a compound melting at 110—112°, probably desylmesityl oxide, when benzoïn is treated with mesityl oxide in presence of potassium cyanide. F. S. K.

The Fluoresceïn Group. By R. Meyer and E. Saul (*Ber.*, 25, 3586—3590).—The compound obtained by distilling hydrofluoranic acid with soda-lime and zinc-dust (Abstr., 1892, 1228) is diphenylenephenylmethane, $CHPh<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$ (m. p. 145°). When fluoran is distilled with zinc-dust, *diphenylenephenylmethane oxide*,

$$CHPh<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>O,$$

is obtained; it crystallises in large rhombohedra, melts at 135—137°, and dissolves readily in ether and benzene, the solutions not exhibiting fluorescence. A second compound, $C_{20}H_{12}O$, may also be isolated; it crystallises in golden-yellow leaflets, melts at 150—152°, dissolves in ether, forming a solution which exhibits a strong, green fluorescence; and is probably a phenylanthranol. A third compound was also produced in the interaction, but its amount was so small that it precluded its examination. Fluoran and diphenylphthalide yield crystalline derivatives with phenylhydrazine; these are being investigated.

A. R. L.

Action of Bleaching Powder and of Hypochlorous acid on Quinones. By T. Zincke (*Ber.*, **25**, 3599—3607; compare Abstr., 1892, 720, 857, and 859).—These experiments relate to α-naphthaquinone. *αα-Diketotetrahydronaphthalene oxide*, $C_6H_4<\begin{matrix}CO\cdot CH\\ CO\cdot CH\end{matrix}>O$, is obtained by mixing α-naphthaquinone with an excess of bleaching powder solution; after a while the mixture becomes warm, and at the end of 24 hours the flocculent, white product is collected, washed, and crystallised from 50 per cent. acetic acid, when it separates in long, white needles, melts at 136°, and is sparingly soluble in ether. Isonaphthazarin (Abstr., 1892, 494 and 720) is formed when it is heated with water at 130—140°, whilst hydroxy-α-naphthaquinone is produced on treatment with aqueous alkalis. The last-named compound is obtained together with chlorhydroxy-α-naphthaquinone when the oxide is heated with dilute hydrochloric acid. *Chlorhydroxyhydro-α-naphthaquinone* (m. p. 142—143°) is furnished on boiling the oxide, dissolved in 50 per cent. acetic acid, with stannous chloride and hydrochloric acid. When an excess of aniline is added

to an alcoholic solution of the oxide, *anilidohydroxydiketotetrahydronaphthalene*, $C_6H_4<\begin{matrix}CO\cdot CH\cdot OH\\ CO\cdot CH\cdot NHPh\end{matrix}$, is obtained, together with Plagemann's anilidohydroxy-α-naphthaquinone (m. p. 210°). The former crystallises in needles of a golden lustre, and is converted into the latter when boiled with alcohol. Attempts to prepare the anilidohydroxyquinone from isonaphthazarin were unsuccessful, but when the former is heated with bromine and acetic acid, it is converted into tribromaniline and isonaphthazarin, a fact which favours the view that the latter is a derivative of α-naphthaquinone. When αα-diketotetrahydronaphthaquinone oxide is dissolved in 50 per cent. acetic acid, and treated with aniline, *hydroxy-α-naphthaquinoneanilide*, $C_6H_4<\begin{matrix}CO\text{ —— }C\cdot NHPh\\ C(NPh)\cdot CH\end{matrix}$, a blue compound melting at 240°, is obtained; whilst if the reaction be conducted in glacial acetic acid solution, anilido-α-naphthaquinoneanilide (m. p. 190°) is an accompanying product. A. R. L.

Derivatives of the β-Naphtholcarboxylic acid melting at 216°. By N. Rosenberg (*Ber.*, **25**, 3634—3635).—*Ethyl β-hydroxynaphthoate* crystallises in radiating needles, melts at 85°, boils at 290—291° without decomposition, and gives a dark green coloration with ferric chloride.

β-Hydroxynaphthamide, $OH\cdot C_{10}H_6\cdot CONH_2$, is obtained by heating the ethyl salt with alcoholic ammonia at 170°. It separates from acetic acid in beautiful crystals, and melts at 185°.

β-Hydroxynaphthomethylanilide, $OH\cdot C_{10}H_6\cdot CO\cdot NMePh$, is obtained by adding phosphorus trichloride to a mixture of β-naphtholcarboxylic acid and methylaniline. It melts at 150°, and gives a green coloration with ferric chloride. E. C. R.

α-Naphtholsulphonic acids. By M. Conrad and W. Fischer (*Annalen*, **273**, 102—117).—The authors have examined the products of the direct sulphonation of α-naphthol, in order to clear up various conflicting statements relative to the nature and properties of the acids so formed.

When α-naphthol is heated at 50° for two hours with concentrated sulphuric acid (2 parts), the principal product is α-naphtholdisulphonic acid [$OH : (SO_3H)_2 = 1 : 2 : 4$], only a small quantity of the monosulphonic acid [$OH : SO_3H = 1 : 2$] being formed.

When a solution of α-naphthol (2 parts) in glacial acetic acid (1 part) is heated for about an hour with concentrated sulphuric acid (2 parts) at 45—50°, about half of the α-naphthol is not acted on, the remainder being for the most part converted into a mixture of 1 : 2- and 1 : 4-naphtholsulphonic acids, which can be readily separated by means of their potassium salts.

Potassium 1 : 2-naphtholsulphonate, $OH\cdot C_{10}H_6\cdot SO_3K + \frac{1}{2}H_2O$, crystallises from water in lustrous prisms, and is only very sparingly soluble in boiling alcohol; 100 parts of water at 18° dissolve about 2·7 parts of the salt, but on the addition of sodium chloride, potassium

chloride, &c., the organic salt is almost completely precipitated. The sodium salt crystallises in prisms or needles, and is soluble in boiling alcohol. The barium salt and the lead salt both crystallise with 1 mol. H_2O.

Potassium nitrosonaphtholsulphonate [O : SO_3K : NOH = 1 : 2 : 4] forms dark red crystals, and its aqueous solution gives a reddish-brown precipitate with ferric chloride; on treatment with warm dilute nitric acid, it yields dinitronaphthol. The corresponding *silver* salt has the composition $C_{10}H_6NO_2{\cdot}SO_3Ag + H_2O$. The *aniline* salt is a yellow, crystalline compound; when heated with aniline at 130—140°, it gives a dark red, crystalline substance, probably naphthaquinonedianilide, which melts at 180°, and has the composition $C_{22}H_{16}N_2O$.

Amidonaphtholsulphonic acid [OH : SO_3H : NH_2 = 1 : 2 : 4], prepared by reducing the nitroso-acid, crystallises in needles, and is identical with the compound described by Seidel (Abstr., 1892, 721).

The alkali salts of 1 : 4 naphtholsulphonic acid are readily soluble in water, and are not precipitated from the solution on adding potassium chloride or alcohol. When a few particles of the potassium salt are treated with cold dilute nitric acid, it yields a dark red solution at first, but afterwards a dark flocculent precipitate is formed; the potassium salt of the 1 : 2-acid, under the same conditions, gives a transient blood-red solution, from which a yellow, resinous substance quickly separates.

The *potassium* salt of nitrosonaphtholsulphonic acid obtained from the 1 : 4-sulphonic acid crystallises in yellow plates, and is readily soluble in hot water; the corresponding silver salt, $C_{10}H_6NO_5SAg$, separates from hot water in crystals. F. S. K.

Dinaphthoxanthen (Methylenedinaphthylene Oxide). By W. Wolff (*Ber.*, **26**, 83—86).—Dihydroxy-β-dinaphthylmethane, $CH_2(C_{10}H_6{\cdot}OH)_2$, can be obtained by adding 40 per cent. formaldehyde to a solution of β-naphthol in a mixture of dilute hydrochloric acid and alcohol; it melts at 194°, not at 188—189°, as stated by Abel (this vol., i, 172). The *diacetyl* derivative, $C_{23}H_{20}O_4$, crystallises in colourless needles, and melts at 211°.

Dinaphthoxanthen, $CH_2<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$, is formed when the preceding compound is heated with toluene and phosphorus oxychloride at 110°; it crystallises in colourless needles, or prisms, melts at 199°, and dissolves in concentrated sulphuric acid, yielding a yellowish-green solution, which shows a green fluorescence.

Tetrahydroxydinaphthylmethane, $CH_2[C_{10}H_5(OH)_2]_2$, prepared by treating dihydroxynaphthalene [$(OH)_2$ = 2 : 7] with formaldehyde and dilute hydrochloric acid, crystallises in colourless needles, turns brown at 230°, and melts at 252° with decomposition; it dissolves in concentrated sulphuric acid, yielding a yellow solution, which quickly turns red on exposure to the air. The *tetracetyl* derivative, $C_{29}H_{24}O_8$, crystallises in needles, and melts at 249·5°. F. S. K.

Action of Sulphuric acid on Citrene. By G. Bouchardat and J. Lafont (*Compt. rend.*, **115**, 1083—1085).—When 146 grams of monhydrated sulphuric acid is added gradually to 1330 grams of citrene (b. p. 175—178°; $[\alpha]_D = +72{\cdot}40$) there is at first considerable development of heat, and the liquid must be cooled, but the addition of the second half of the acid does not increase the temperature of the mixture. After remaining for 24 hours, only very minute quantities of sulphurous anhydride are given off, but the whole of the citrene has disappeared, and the products are optically inactive. On washing with water, it is found that 140 grams of the sulphuric acid out of the 146 remain in the free state, and the water contains no sulphonic acid. The product contains cymene and a hydrocarbon which seems to be pseudocumene, both of which probably pre-exist in the citrene, but the greater part boils at 310—320°, and consists of diterpilene or colophene. There is also a residue which solidifies when cold, and which consists of higher polymerides of citrene. It follows that the action of sulphuric acid on citrene furnishes solely higher polymerides of that hydrocarbon, the most abundant being diterpilene. This result explains the formation of diterpilene in the preparation of terebene or inactive camphene. One of the products of the action of sulphuric acid on terebenthene is a lævogyrate terpilene boiling at 178°, and physically isomeric with citrene, and probably this terpilene, by the action of further quantities of sulphuric acid, is converted into an inactive diterpilene, identical with that derived from citrene. C. H. B.

A Crystalline Dihydrochloride from Eucalyptus Oil. By Anthoine (*J. Pharm.* [5], **26**, 391—394).—By acting with gaseous hydrogen chloride on those portions of eucalyptus oil which boil between 150° and 178°, a crystalline dihydrochloride, $C_{10}H_{16},2HCl$, is obtained, which melts at 50°, boils at 115°, and has properties similar to those of the dihydrochloride obtained from oil of turpentine. Small amounts act as antiseptics to putrescible solutions, but do not hinder the action of enzymes. T. G. N.

American Menthol. By J. H. Long (*J. Amer. Chem. Soc.*, **14**, 149—150).—Japanese menthol crystallises in small prisms, thus differing from American menthol, which forms long needles. After careful purification, American menthol melts at 42·3°, boils at 212·5° (corr.) under 742 mm. pressure, and has in the crystalline state, a sp. gr. = 0·890 at 20°/4°, and when fused, a sp. gr. = 0·8810 at 44·6°/4°. The rotatory power of menthol in alcoholic solution at 20° is expressed, for concentrations between 8 and 70 per cent. of menthol, by the equation $[\alpha] = 48{\cdot}247° + 0{\cdot}011108q + 0{\cdot}00001870q^2$, where q is the percentage of inactive solvent present. For solutions in benzene, not too dilute, the equation $[\alpha] = 49{\cdot}511° + 0{\cdot}025634q + 0{\cdot}0008403q^2 - 0{\cdot}00001102q^3$ applies, whilst for solutions in acetic acid, the equation is $[\alpha] = 47{\cdot}711° + 0{\cdot}006386q + 0{\cdot}00007142q^2$. Fused menthol has the rotatory power $[\alpha]_D = -49{\cdot}86°$. The comparison of the physical properties of American with those of Japanese

menthol shows only very slight differences, which are probably due to a slight admixture with menthone in the former case.

A. J. G.

Amine from Dextromenthone. By A. NEGOVOROFF (*J. Russ. Chem. Soc.*, **23**, 443—446).—Dextromenthone, $[\alpha]_D = +21{\cdot}6°$, was prepared by Beckmann's method from menthol, m. p. 43°, and transformed into the corresponding oxime by the action of hydroxylamine and sodium hydrogen carbonate in alcoholic solution. The oxime had the specific rotation $[\alpha]_D = -9{\cdot}21°$. 17·5 grams, on reduction in alcoholic solution with metallic sodium, gave 7 grams of the crude amine, $C_{10}H_{19}{\cdot}NH_2$, about 40 per cent. of the theoretical yield. The following table exhibits the properties of this amine compared with those of the amine from lævomenthol oxime:—

	Amine from	
	Lævomenthol.	Dextromenthol.
Boiling point	206—207°	206—207° (at 747 mm.)
Sp. gr. 0°/0°	0·8685	0·8749
$[\alpha]_D$	−33·60	−9·26
Hydrochloride	long tables, rhombic	prismatic needles, rhombic
$(C_{10}H_{19}NH_2)_2H_2PtCl_6$	golden-yellow scales	yellow silky needles

J. W.

Occurrence of Bornyl Acetate in the Ethereal Oils of Abies sibirica and Abies pectinata. By E. HIRSCHSOHN (*Chem. Centr.*, 1892, ii, 793; from *Pharm. Zeit. Russ.*, **30**, 593—595).—The author has isolated bornyl acetate from the ethereal oil of *Abies sibirica*, of which it forms 30 per cent.; this oil is therefore the best material for the preparation of borneol. The substance which Spehr obtained from oil of pine needles, and described as a terpene hydrate, is in reality bornyl acetate. The ethereal oil of *Abies pectinata* also contains bornyl acetate, which may also be assumed to be present in oil of *Pinus canadensis*.

A. J. G.

Gutta-percha. By O. OESTERLE (*Arch. Pharm.*, **230**, 641—674).—Gutta-percha was boiled with successive fresh quantities of water, until the latter was no longer coloured; by this means a tannin, sugar, and (inorganic?) salts were extracted; it was then dried, repeatedly extracted with boiling alcohol, and the alcoholic extract slowly cooled; *alban* then separated out as a white, crystalline precipitate, and the mother liquor from this, when evaporated, left a brown, resinous mass of impure *fluavil*, smelling like colophony. The residual gutta-percha was then dissolved in chloroform, the solution filtered from a small residue, and mixed with alcohol; *gutta* then separated in the form of a milky emulsion, which gradually gathered into flakes. At the same time, a stringy substance, *guttan*, was precipitated; it is, however, very unstable, for when it is

repeatedly dissolved in chloroform and precipitated with alcohol, it is gradually converted into gutta; it differs from the latter in containing oxygen.

Gutta, $(C_{10}H_{16})_n$, is a white, amorphous substance with high molecular weight, and melts at 53°. Bromine attacks it, with evolution of hydrogen bromide; it is also gradually affected by air and light, becoming yellow and friable, and partially soluble in alcohol, aqueous potash, and benzene. It is stable in the absence of light and air.

Alban, $C_{40}H_{64}O_2$, melts at 195° (uncorr.). It is attacked by bromine, with evolution of hydrogen bromide, and by nitric acid, with formation of a nitrogenous substance, but hydroxylamine and phenylhydrazine do not attack it, neither can an acetyl derivative be prepared. When distilled with phosphorus pentasulphide, it yields an oil which contains sulphur; distilled with zinc-dust, it yields liquid hydrocarbons, on which nitric acid acts, producing substances with an odour of flowers and of musk. When heated with alcoholic potash for 24 hours at 150° in a sealed tube, a hydrocarbon, *albene*, is obtained.

Fluavil, $(C_{10}H_{16}O)_n$, is a yellow, amorphous substance, melting at 82—85°; no derivative could be prepared.

The above-mentioned substances were all contained in commercial gutta-percha, and also in two samples collected exclusively from *Payena Leerii*. Of the latter, which were originally equally plastic, one had become brittle; this one was found to contain more fluavil. Gutta appears to be the essential constituent of gutta-percha, and to it the plastic properties of the latter are due. Alban is present in considerable quantity, but does not appear to materially affect these properties. Fluavil is usually present in small amount; a larger proportion of it spoils the gutta-percha, rendering it brittle and friable. All these constituents of gutta-percha are chemically inert—except that gutta (and guttan) are slowly affected by light; to this the gradual deterioration in the quality of gutta-percha when kept is doubtless to be ascribed. C. F. B.

Brazilin Methyl Ether. By C. Schall (*Ber.*, **25**, 3670—3672).—The author has repeated his analyses of brazilin methyl ether and of a number of bromine derivatives in order to prove whether the compound contains three or four methoxyl groups; it appears to form a tetracetyl derivative, the investigation of which is to be continued. J. B. T.

Jalapin. By T. Poleck (*Chem. Centr.*, 1892, ii, 786—787; from *Zeit. österr. Apoth.-vereins*, 1892, 1—14).—Much of this paper consists of a recapitulation of earlier work (Abstr., 1885, 669). Samelson's jalapinole (*loc. cit.*) does not exist. When jalapin is hydrolysed with hydrochloric acid, it yields dextrose and jalapinolic acid, which has the formula $C_{16}H_{30}O_3$ (not $C_{16}H_{30}O_4$, as previously stated). It is odourless, crystallises in tufts of white needles, and melts at 63—64°. The formula was confirmed by analyses of the silver, barium, and ethyl salts. A. J. G.

Names of New Remedies. By J. D. Riedel (*Chem. Centr.*, 1892, ii, 584—586; from *Apoth.-Zeit.*, **7**, 405—406).—A list of the

names under which various organic chemicals have been recently introduced as drugs.

Opium Smoke. By H. Moissan (*Compt. rend.*, **115**, 988—992).—The opium specially prepared for smoking, or *chandoo*, is dried immediately before use, at a temperature that does not exceed 240°, and is smoked at a temperature of about 250°. Combustion of *chandoo* in a current of air at 250° produces only a small quantity of fragrant oils, and a small quantity of morphine, which is probably carried forward by the water vapour.

The *dross*, or residue left when *chandoo* is smoked in this way, is used, together with more or less adulterated opium, by the less wealthy smokers. Combustion of the *dross* and the adulterated opium requires a temperature not lower than 300°, and in this case the decomposition is more complicated, and the volatile products contain pyrroline, acetone, and hydropyridic and pyridic bases (compare next abstract and this vol., ii, 179). C. H. B.

Tobacco Smoke. By A. Gautier (*Compt. rend.*, **115**, 992—993).—Researches, which will shortly be described in detail, show that when tobacco is smoked in a pipe, the volatile liquid products chiefly consist of basic compounds. They contain a large proportion of nicotine, a higher homologue of nicotine, $C_{11}H_{16}N_2$, which pre-exists in tobacco leaves, and a base, C_6H_7NO, which seems to be a hydrate of picoline. Other less volatile bases, including hydropyridines, are also formed. These alkaloïds result from the decomposition, at a comparatively low temperature, of the carbopyridic and carbohydropyridic or analogous acids present in the tobacco. C. H. B.

Constitutions of the Methylpyrrolines. By C. U. Zanetti (*Gazzetta*, **22**, ii, 269—276).—The methylpyrroline boiling at 148—150° yields, with hydroxylamine hydrochloride, a dioxime, $C_5H_8(NOH)_2$, which crystallises in lustrous, white scales melting at 73—74°; it is very soluble in all the ordinary solvents, with the exception of light petroleum. Inasmuch as it gives a ketonic acid on treatment with potash, it is most probably the dioxime of levulinic aldehyde, and the pyrroline from which it is derived must be α-methylpyrroline (compare Zanetti, Abstr., 1892, 74).

The methylpyrroline which boils at 142—143°, obtained by Dennstedt's method (Abstr., 1891, 1501), when treated with hydroxylamine hydrochloride, yields the dioxime melting at 73—74°, and a small quantity of a substance melting at 159—160°. The latter is probably derived from β-methylpyrroline, but owing to the small quantity of it obtained, no analysis could be made. W. J. P.

Action of Propyl Alcohol on Pyrroline. By M. Dennstedt (*Ber.*, **25**, 3636—3637).—When a mixture of propyl alcohol and pyrroline is distilled over heated zinc-dust, a product is obtained which may be divided, by fractional distillation, into five fractions.

Fraction 1, boiling at 173—175°, has the properties and composition of a *c*-propylpyrroline, C_7NH_{11}, and is a bright oil, which quickly turns

yellow on exposure to light. The acetyl compound, obtained by the action of acetic anhydride, boils at 270°. The *c*-propylcinnamylpyrroline, obtained by the action of benzaldehyde, crystallises in yellow needles, and melts at 148—150°, whilst the *n*-acetylpropylpyrroline is a dark yellow, viscid oil, and boils at 245°. When an ethereal solution of the propylpyrroline is treated with dry hydrogen chloride, dipropyldipyrroline hydrochloride is obtained; and on treating this salt with sulphuric acid, it is converted into dipropylindole. The latter boils at 305°, and gives a picrate melting at 98—100°.

Fraction 2 boils at 185—187°, and has also the properties and composition of a *c*-propylpyrroline. The *c*-acetyl compound boils at 275°. The *n*-acetyl compound boils at 250°. The propylcinnamylpyrroline crystallises from alcohol in lustrous cubes, and melts at 161—162°. The dipropylindole boils at 290°.

Fraction 3 boils at 205—210°, and is a *c*-dipropylpyrroline. The *c*-acetyl compound boils at 270—280°, the *n*-acetyl compound at 250—260°.

The last two fractions, boiling at 270—280° and 300—310°, are isomerides of the mesitylpyrroline and phoronpyrroline obtained from acetonepyrroline. E. C. R.

Trimethyltetrahydroquinoline. By A. Ferratini (*Gazzetta*, **22**, ii, 417—422; compare Abstr., 1892, 614).—Trimethyldihydroquinoline is readily reduced by tin and hydriodic acid, with production of trimethyltetrahydroquinoline; the *hydriodide* of the latter, $C_9NH_8Me_3,HI$, forms small, white prisms, which melt at 197°. The methiodide, when distilled with potash, merely loses methyl iodide, giving the free base. On heating trimethyltetrahydroquinoline with hydriodic acid and red phosphorus in closed tubes at 250°, methyl iodide is obtained, together with a base which seems to be *dimethyltetrahydroquinoline*, $C_9NH_8Me_2$, as it gives a *nitronitrosamine*, $C_{11}H_{13}N(NO)\cdot NO_2$, with nitrous acid. This substance crystallises in large, thin, transparent, yellow plates, melts at 154—155° with slight decomposition, and gives Liebermann's reaction. W. J. P.

Tetrahydroisoquinoline. By A. Ferratini (*Gazzetta*, **22**, ii, 422—430; compare preceding abstract).—Tetrahydroisoquinoline reacts energetically with methyl iodide, yielding a mixture of methyltetrahydroisoquinoline hydriodide and *methiodide*, $C_{10}H_{13}N,MeI$; the latter forms white scales, melts at 189°, and turns yellow on exposure to the air. On treating it with silver chloride suspended in water, a solution is obtained which yields an *aurochloride* of the composition $C_{11}H_{15}N,HAuCl_4$; this forms lustrous, yellow laminæ, and melts at 184—185°; the corresponding *platinochloride*,

$$(C_{11}H_{15}N)_2,H_2PtCl_6,$$

forms beautiful, yellow needles melting at 228° with decomposition.

On heating methyltetrahydroisoquinoline methiodide with potash, a base distils, which, when suitably purified, combines with methyl iodide with development of heat, forming a *methiodide* of the composition $C_{13}H_{18}NI$. This is obtained in long, rectangular plates melt-

ing with decomposition at 200—201°; on distillation with potash, it yields a base, which gives a yellow, crystalline *aurochloride* melting at 105°. W. J. P.

Synthesis of Isoquinoline Derivatives. By S. GABRIEL and A. NEUMANN (*Ber.*, **25**, 3563—3573; compare Abstr., 1887, 1112).—*Diacetylorthocyanobenzyl cyanide*, $CN\cdot C_6H_4\cdot CAc_2\cdot CN$, forms small, lustrous needles, melts at 137—138°, and when heated with 75 per cent. acetic acid saturated with hydrogen chloride, yields 3′-*methylisocoumarin* (*isobenzalphthalide*), $C_6H_4<\begin{matrix}CH:CMe\\ |\\ CO\cdot O\end{matrix}$, melting at 73—74°, and isomeric with ethylidenephthalide (Abstr., 1886, 243). On heating the compound with alcoholic ammonia, 3′-*methylisocarbostyril*, $C_6H_4<\begin{matrix}CH:CMe\\ |\\ CO\cdot NH\end{matrix}$, is formed; this crystallises from alcohol in rectangular prisms, and melts at 211°. 3′ : 4′-*Methylcyanisocarbostyril*, obtained by dissolving diacetylorthocyanobenzyl cyanide in warm, dilute alkali hydroxides, forms minute, white needles, melts above 310°, is insoluble in ordinary solvents and ammonia, and gives 3′-*methylisocarbostyril* on being heated with dilute sulphuric acid. 2′ : 3′ : 4′-*Dimethylcyanisocarbostyril* is obtained by methylating 3′ : 4′-methylcyanisocarbostyril; it crystallises in delicate needles, melts at 182—183°, and, when heated with dilute sulphuric acid, yields 2′ : 3′-*dimethylisocarbostyril*, which crystallises in colourless prisms, melts at 103°, and decomposes into 3′-methylisocoumarin and methylamine on being heated at 230° with hydrochloric acid in a sealed tube. 1′ : 3′-*Chloromethylisoquinoline* is produced by boiling 3′-methylisocarbostyril with phosphorus oxychloride; it is volatile with steam, melts at 35—36°, boils at 280—281° (757 mm.), and when heated in a sealed tube with hydriodic acid and phosphorus, furnishes 3′-*methylisoquinoline*. The latter melts at 68°, boils at 246° (761 mm.), and is volatile with steam; the *platinochloride* melts at 195°, and the *picrate* at 197—198°. When a mixture of 3′-methylisocarbostyril and zinc-dust is heated to a dull red heat in a current of hydrogen, 3′-methylisoquinoline distils over.

3′ : 4′-*Phenylcyanisocoumarin*, $C_6H_4<\begin{matrix}C(CN):CPh\\ |\\ CO\text{—}O\end{matrix}$, is obtained by heating orthocyanobenzyl cyanide with benzoic chloride; it forms a citron-yellow, microcrystalline powder, melts at 204—205°, is sparingly soluble in hot alcohol, and yields isobenzalphthalide (Abstr., 1885, 1231) when heated at 180° with 75 per cent. acetic acid saturated with hydrogen chloride, and 3′ : 4′-*phenylcyanisocarbostyril*, when heated at 180° with alcoholic ammonia; the latter crystallises in lemon-yellow needles, melts at 270°, and is sparingly soluble in alcohol. 3′-Phenylisoquinoline is more easily prepared by distilling a mixture of 3′-phenylisocarbostyril and zinc-dust in a current of hydrogen than by the method formerly given (Abstr., 1886, 226). A. R. L.

Preparation and Properties of Methyloxythiazole. By J. TCHERNIAC (*Ber.*, **25**, 3648—3652).—Methyloxythiazole is readily

prepared by the action of sodium hydrogen carbonate on thiocyanacetone in aqueous solution at the ordinary temperature; the clear liquid, after separation from resinous products, is repeatedly extracted with boiling ether in an apparatus devised by the author, a sketch of which is given in the original paper. The yield is 41·6 per cent. of the theoretical. The thiazole crystallises in pale, cream-coloured needles or prisms melting at 105—106°, and solidifying at 97—98°. A molecular weight determination by Raoult's method proves that the substance has the simple formula C_4H_5SNO. J. B. T.

The Pyrazoline Reaction. By L. KNORR (*Ber.*, **26**, 100—103).—Pyrazoline bases derived from phenylhydrazine, when treated with oxidising agents in acid solution, are converted into magenta-red to blue dyes, and by this reaction very small quantities of pyrazolines can be detected. The reaction is equally applicable to pyrazoles derived from phenylhydrazine, if they are first reduced with sodium and alcohol to the corresponding pyrazoline.

This reaction is applicable to pyrazoles derived from phenylhydrazine which do not contain oxygen, and also to derivatives of 1-phenylpyrazole. Pyrazolones derived from phenylhydrazine do not, as a rule, give this reaction, but 1-phenyl-3:4-trimethylpyrazolone is an exception. The pyrazolones obtained from hydrazine hydrate do not give the reaction, even if they contain a benzene residue substituted in the pyrazole nucleus. Thus pyrazole and its homologues, phenylmethylpyrazole (from benzoylacetone and hydrazine hydrate), and 3:5-diphenylpyrazole (from dibenzoylmethane and hydrazine) do not give the reaction. The reaction seems to be determined by the presence of a benzene residue in the position 1.

The author has obtained a compound of the formula

$$\begin{matrix} N-NPh \\ \| \\ CMe\cdot CH_2 \end{matrix}\!\!>\!CH\cdot CH\!<\!\!\begin{matrix} NPh\cdot N \\ \| \\ CH_2\cdot CMe \end{matrix}$$

by the careful oxidation both of 1-phenyl-3-methylpyrazoline and of 1:5-diphenyl-3-methylpyrazoline. In the case of the latter compound, the condensation takes place with elimination of the 5-phenyl group. It crystallises from acetic acid in characteristic silvery leaflets, melts at 275—278°, and dissolves in mineral acids with a magenta coloration. E. C. R.

Pyrazole Derivatives from Unsaturated Acids and Hydrazines. By L. KNORR and P. DUDEN (*Ber.*, **26**, 103—108, 109—111).—The authors have already described (Abstr., 1892, 731) 1 : 3 : 5-phenylmethylpyrazolidone. The 2-*acetyl derivative* crystallises in needles easily soluble in boiling water, alcohol, glacial acetic acid, and ether, and melts at 126°. The 2-*benzoyl derivative* crystallises in plates insoluble in water, and melts at 162°. The 2-*nitroso-derivative* forms pale-yellow needles melting at 54—55°, and is very unstable, being readily reconverted into the pyrazolidone by reducing agents. A *methiodide* of the pyrazolidone was also obtained; it decomposes at 310° without previous fusion.

The pyrazolidone is easily reduced by the action of sodium and

alcohol, phenylmethylpyrazolidine and *phenylmethylpyrazoline* being formed. The latter is a feeble base, its salts being decomposed by water, and is volatile in steam; it is not oxidised by mercuric oxide, or by Fehling's solution. It melts at 72—74°, and boils at 289° under 757 mm. pressure. The authors also prepared it by the reduction of 1 : 3-phenylmethylpyrazole.

In order, if possible, to determine whether the space configuration of the unsaturated acids influences their condensation with hydrazines, the action of the liquid isocrotonic acid on phenylhydrazine was studied. The same pyrazolidone of m. p. 84° was obtained as from the solid acid, although the yield was much less. As, however, J. A. Wislicenus has now shown (*Inaug. Dissert.*, Leipzig, 1892) that the liquid acid is probably a molecular mixture of the two geometrically isomeric modifications, the results obtained leave the point in question unsettled.

The authors have further investigated the compound $C_{15}H_{12}N_2O$, previously obtained by Knorr by the distillation of the hydrazide of cinnamic anhydride (Abstr., 1887, 665). By treatment with phosphorus pentasulphide, it is reduced to 1 : 5-diphenylpyrazole (see next abstract) of m. p. 55°, and is therefore 1 : 5 : 3-diphenylpyrazolone, $NPh<\begin{matrix}NH\cdot CO\\ CPh\cdot CH\end{matrix}$. When heated with excess of methyl iodide, it yields 1 : 5 : 2 : 3-*diphenylmethylpyrazolone*; this is sparingly soluble in cold, but easily in boiling water, also in alcohol and in chloroform. It crystallises in scales melting at 139°, and is more basic than diphenylpyrazolone; its *picrate* forms needles melting at 180—181°. A solution of the base in strong sulphuric acid is coloured cherry-red by the addition of a drop of potassium dichromate solution.

L. T. T.

Isomerism of the Diphenylpyrazoles and of the Pyrazole Derivatives from Ethyl Benzoylacetoacetate and Ethyl Benzalacetoacetate. By L. Knorr and P. Duden (*Ber.*, **26**, 111—116).—The authors have re-examined the various diphenylpyrazoles to establish their constitution and to reconcile the various conflicting statements concerning them.

1 : 5-Diphenylpyrazole melts at 55° and boils at 337° under 736 mm. pressure. It is the pyrazole which has been obtained (1) from cinnamic acid (see preceding abstract), (2) from benzoylpyruvic acid (Beyer and Claisen, Abstr., 1887, 943), (3) from benzoylaldehyde (Claisen and Fischer, Abstr., 1888, 690), (4) from diphenylpyrazoledicarboxylic acid (Knorr and Laubmann, Abstr., 1889, 409), and (5) from ethyl phenylacetoacetate (Bischler, this vol., i, 44). The corresponding 1 : 5-diphenylpyrazoline melts at 136—137°.

1 : 3-*Diphenylpyrazole* melts at 84°, boils at 341—342° under 270 mm. pressure, and forms glistening, white crystals. It has been obtained by the authors from ethyl benzoylacetoacetate, from 1 : 3-diphenylpyrazole-4 : 5-dicarboxylic acid (from ethyl benzalacetoacetate) and from benzoylaldehyde. Whilst Claisen and Fischer obtained from benzoylaldehyde the pyrazole melting at 55°, the authors only obtained that melting at 84°. Apparently slight modifications of the conditions of experiment cause a difference in the direction of the

reaction. The corresponding 1 : 3-diphenylpyrazoline melts at 104°, but not sharply.

3 : 5-*Diphenylpyrazole* melts at 200° and boils at 347° under 155 mm. pressure, is crystalline, and does not form a pyrazoline. The authors have prepared this pyrazole from dibenzoylmethane.

1 : 3-*Diphenylpyrazole*-4 : 5-*dicarboxylic acid*, $N<\begin{matrix}NPh\cdot C\cdot COOH\\ \|\\ CPh\cdot C\cdot COOH\end{matrix}$, was obtained by the oxidation of diphenylmethylpyrazolecarboxylic acid; it melts at 190°. Its *barium salt* crystallises in needles. At 200—250°, the acid gives off carbonic anhydride, and yields 1 : 3-diphenylpyrazole. L. T. T.

Pyrazoles from Unsaturated Acids and Hydrazines. By P. Duden (*Ber.*, **26**, 117—122).—The author has extended his previous work to bibasic unsaturated acids containing, or probably containing, the group -CH:CH·COOH. Both maleïc and fumaric acids, when heated at 110° with one equivalent of phenylhydrazine, yielded 1 : 5 : 3-*phenylpyrazolidonecarboxylic acid*, $NPh<\begin{matrix}NH\cdot CH\cdot COOH\\ |\\ CO\cdot CH_2\end{matrix}$, which is sparingly soluble in cold water, crystallises in concentrically grouped needles, and melts with partial decomposition at 201—202°. Its *sodium salt* is amorphous and deliquescent; its *silver salt* forms a white precipitate, which deposits silver when boiled with water. The acid reduces Fehling's solution, mercuric oxide, ferric chloride, &c. By careful oxidation with ferric chloride, it yields 1 : 5-phenylpyrazolonecarboxylic acid, melting at 265°, and described by W. Wislicenus (*Ber.*, 1887, 234). In glacial acetic acid solution, the formation of a pyrazolidone does not take place, fumaric acid remaining unchanged, and maleïc acid yielding maleÿlphenylhydrazine (Hotte, Abstr., 1887, 671). When fumaric or maleïc acid is heated with excess (three equivalents) of phenylhydrazine, *phenylhydrazinesuccinyldihydrazide*, $N_2H_2Ph\cdot C_2H_3(CO\cdot N_2H_2Ph)_2$, is formed. This substance is insoluble in water and ether, and but sparingly soluble even in boiling alcohol; it crystallises in needles, and melts at 199—200°. Strong alkalis or acids resolve it into 1 : 5 : 3-phenylpyrazolidonecarboxylic acid and phenylhydrazine.

Oleïc acid yields a *hydrazide*, $C_{24}H_{40}N_2O$, which forms crystals melting at 72—73°, and elaïdic acid a *hydrazide*, $C_{24}H_{40}N_2O$, which crystallises in needles melting at 98—99°, but from neither acid could a pyrazole derivative be obtained. The author considers it probable, therefore, that neither of these acids contains the group -CH:CH·COOH. L. T. T.

Action of Hydriodic acid on Cinchonidine. By G. Neumann (*Monatsh.*, **13**, 651—662; compare Skraup, Abstr., 1892, 83).—*Trihydriodocinchonidine*, $C_{19}H_{22}N_2O,3HI$, is obtained by heating cinchonidine with five times its weight of hydriodic acid (sp. gr. 1·7) for 2½ hours. It crystallises in yellowish-white needles, which become transparent at 140°, and melt, with decomposition, at 216°. When decomposed with 1 and 2 mol. proportions respectively of alcoholic ammonia, it gives rise to the compounds $C_{19}H_{22}N_2O,2HI$ and

$C_{19}H_{22}N_2O,HI$. Of these, the former is pale yellow, melts at 184°, and decomposes with evolution of gas at 221°; the latter melts at 166°, forms a sulphate, $C_{19}H_{22}N_2O,HI,H_2SO_4$, and when boiled with alcoholic potash yields *β-cinchonidine*, $C_{19}H_{22}N_2O$.

β-Cinchonidine crystallises from alcohol in plates, melts at 244°, and gives the following salts:—The *oxalate*, $C_{19}H_{22}N_2O,H_2C_2O_4$, crystallises in colourless needles, which melt at 118° and decompose at 151°; the *tartrate*, $C_{19}H_{22}N_2O,C_4H_6O_6$, melts with decomposition at 218°; and the two *platinochlorides*, $C_{19}H_{22}N_2O,H_2PtCl_6$ and $2C_{19}H_{22}N_2O,H_2PtCl_6$. On heating with hydriodic acid, *β*-cinchonidine gives the above-described trihydriodocinchonidine, melting at 216°. The latter is converted by silver nitrate into *γ-cinchonidine*, which melts at 238°, does not give such characteristic salts as *β*-cinchonidine, and forms the two platinochlorides $C_{19}H_{22}N_2O,H_2PtCl_6$ and $2C_{19}H_{22}N_2O,H_2PtCl_6$. On distillation with water, trihydriodocinchonidine yields a product which has the aldehydic property of reducing ammoniacal silver nitrate.

G. T. M.

Sparteïne. By F. B. Ahrens (*Ber.*, **25**, 3607—3612).—An aqueous solution of oxysparteïne (Abstr., 1891, 842) reduces Fehling's solution on being warmed with it. The *hydrochloride* crystallises with 1 mol. H_2O, and melts above 230°; from more dilute solutions, however, it separates with 4 mols. H_2O; the crystals are completely dehydrated at 160°, not, however, without partial decomposition. The *hydrobromide* crystallises with $3\frac{1}{2}$ mols. and with $2\frac{1}{2}$ mols. H_2O, and the *hydriodide* crystallises with 1 mol. H_2O. The *nitrate* forms large, transparent tables (with 1 mol. H_2O), sinters at 202°, and melts at 207°. The *methiodide*, $C_{15}H_{24}N_2O,MeI$, crystallises in yellowish needles, and melts at 191—193°; on adding freshly precipitated silver chloride to its aqueous solution, the *methochloride* is obtained. The latter yields a *platinochloride*, $C_{15}H_{24}N_2O,HMePtCl_6 + H_2O$, which forms transparent red crystals, and melts at 228—229°, and an *aurochloride* melting at 190—191°. Oxysparteïne is not attacked when heated at 250° with concentrated sulphuric acid, or when warmed with nitric acid; hydroxylamine and phenylhydrazine are without action on it. When heated at 150° with phosphorus oxychloride, it is converted into an oily *base*, which yields an *aurochloride*, $C_{15}H_{22}N_2,2HAuCl_4$, crystallising in needles, and melting at 160—161°. Hürthle finds that oxysparteïne strengthens the heart's action (see also *Arch. experim. Pathol. Pharm.*, 1892, 141).

Dioxysparteïne, $C_{15}H_{26}N_2O_2$ (Abstr., 1887, 1056), is the ultimate product of the action of hydrogen peroxide on sparteïne. The *hydrobromide* forms colourless crystals, and melts at 146—147°, whilst the *hydriodide* melts at 137°. The free *base* prepared from these salts crystallises in translucent prisms, and melts at 128—129°. The *mercurochloride* melts at 193°.

Trioxysparteïne is obtained by the action of hydrogen peroxide on oxysparteïne; it is crystalline, but has not been prepared quite pure. The *platinochloride*, $(C_{15}H_{24}N_2O_3)_2,H_2PtCl_6 + 3\frac{1}{2}H_2O$, crystallises in orange needles, and decomposes at about 200°; the *aurochloride* forms long, lance-shaped crystals, and melts at 136—137°. The research is proceeding.

A. R. L.

Behaviour of Hydrochloric acid to Albumin in relation to the Chemical Investigation of Gastric Juice. By L. Sansoni (*Chem. Centr.*, 1892, ii, 876—875; from *Berlin klin. Woch.*, **29**, 1043—1045, 1084—1089).—An aqueous solution of albumin has the property of uniting with a certain quantity of hydrochloric acid, so that the acidity of the mixed solution is diminished, and the more concentrated the albumin solution the more acid is thus concealed. This loss can be shown either by the phloroglucinol-vanillin method, or by the employment of phenolphthaleïn. With peptone, it is only in the case of the first of the reagents that part of the acid is not recognisable, and the complete peptonisation of albumin seems to set free any hydrochloric acid previously retained by it; in the intermediate stages of the peptonisation, the loss of acidity is proportional (inversely ?) to the duration of the artificial digestion, and, therefore, to the amount of albumin converted into peptone. A mixture of albumin and hydrochloric acid does not recover the lost acidity when kept for a long time at 38°, even if pepsin is present, provided the conditions are so arranged that much peptonisation does not occur. By the continued action of a temperature of 100—110°, the acidity is partly or wholly lost, but this does not occur with mixtures of peptone with hydrochloric acid.

This combination of albumin with hydrochloric acid does not seem to take place in constant proportion; where the mixture has not been heated to higher temperatures, the greater portion of the hydrochloric acid can be removed by dialysis.

The behaviour at 100—110°, described above, leads to the conclusion that all methods for the estimation of free hydrochloric acid in gastric juice, depending on the evaporation of the gastric juice, must be erroneous, inasmuch as too little free hydrochloric acid will be found.

A. J. G.

Albumoses and Peptone. By W. Kühne (*Zeit. Biol.*, **29**, 1—40).—Solutions containing a mixture of albumoses and peptone give a precipitate of albumoses when saturated with ammonium sulphate, the peptone remaining in solution. After filtration, the filtrate, if set aside, will subsequently give a further precipitate if more salt is added. This has been explained by supposing that the saturation was in the first instance incomplete, or that the peptone is partially changed back into albumose. The present research shows that the former is the more probable explanation. There are many precautions necessary, in order to precipitate the last traces of albumose. It is necessary in the first instance to use large volumes of the saturated solution in addition to merely adding crystals of the salt to the proteïd mixture. Further, it is found that whereas the greater part of the albumose is precipitated by the salt if the reaction of the mixture is made acid, the residue which is difficult of precipitation comes down more readily if the reaction is made alkaline. It is further necessary after the solution of peptone is obtained to remove the salt employed; a method for doing this by the use of barium carbonate after concentration is fully described. If pancreatic juice has been used for the preparation of peptone, care also must be taken that leucine and tyrosine are removed also. In drying, concen-

trating, &c., especially if sulphuric acid is used, a brownish product is formed; this is minimised by care in the manipulations. This substance is precipitable by ammonium sulphate, it is not, however, albumose; it gives no biuret reaction. Further, if a precipitate forms in dialysis, it is not necessarily of proteïd nature; if hard water is used, it may be calcium sulphate.

Pekelharing does not seem to have noticed the necessity of these and other precautions and details, and much of the present paper is polemical, showing Pekelharing's supposed errors, and pointing out that there are more differences between peptones and albumoses than a mere difference of solubility in ammonium sulphate.

Diffusibility of Albumoses and Peptone.—Hetero-albumose is the least diffusible of the albumoses; in neutral saline solutions it is precipitated, and there is no loss in dialysis. Dissolved in ammonia it loses 5·22 per cent. Deutero-albumose comes next (loss 24·1 per cent.); then proto-albumose (loss 28·3 per cent.). Peptone loses 51 to 51·8 per cent.

Koch's tuberculin contains an indole-like substance in addition to albumoses (small quantities of proto-albumose, large quantities of deutero-albumose). In the process of the action of the tubercle bacillus, proto-albumose is first formed, then deutero-albumose. The bacteria so far act like digestive ferments, but there is little or no true peptone formed, and leucine and tyrosine are also absent. Tuberculin also gives a colour with bromine; this substance, tryptophan or proteïnchromogen, is probably a mixture of the indole-like substance with other not fully recognised materials.

The hay bacillus acts somewhat differently when grown in solutions of proto-albumose, for not only are secondary albumoses formed, but also true peptone, tyrosine, leucine, tryptophan, and ammonia. It is thus very like trypsin in its action.

With *Bacillus prodigiosus* very little albumose remains; it is almost entirely broken up into peptone, leucine, tyrosine, tryptophan, and the indole yielding substance.

In no case was there any formation of hydrogen sulphide.

W. D. H.

Certain Chemical Constituents of the Medulla of Nerve. By A. Kossel and F. Freytag (*Zeit. physiol. Chem.*, **17**, 431—456).—Attention is in the present research directed to the cerebrosides, constituents, apparently, of the medullary sheath of nerve fibres, not of the axis cylinders.

The substance called protagon is not a single material, but there is more than one protagon. They yield either one of two, or, perhaps, three, derivatives called cerebrin, kerasin or homocerebrin, and encephalin; and further, probably several lecithins are obtainable from the different protagons. The protagons resemble each other in the following points:—

1. They contain C, H, N, O, P, and, in part, S.
2. By oxidation with nitric acid, they yield higher fatty acids.
3. By the action of boiling sulphuric or hydrochloric acid, reducing carbohydrates are formed.
4. By the action of alkalis they yield cerebrosides, which further

split into ammonia, galactose, and a third complex material, which, on fusion with potash, yields higher fatty acids.

Elementary analysis of protagon crystals, prepared as Gamgee and Blankenhorn direct (*Zeit. physiol. Chem.*, **3**, 260), gave practically the same results as in their and Baumstark's (Abstr., 1885, 918) analyses. The pure crystals yield the two cerebrosides cerebrin and kerasin among their decomposition products. The analyses of these substances agree well with those of Thudichum, Parcus, and others. Their molecular weight was investigated by Beckmann's boiling method and by the analysis of their barium and bromine compounds. They further yield, by treatment with nitric acid, a fatty acid, recognised as neurostearic acid by Thudichum, and correctly analysed but not identified by Müller. It is, in fact, stearic acid, 3 mols. of which are formed from cerebrin for every 2 atoms of nitrogen. From all these considerations the formula given to cerebrin is $C_{70}H_{140}N_2O_{13}$, and to kerasin $C_{70}H_{138}N_2O_{12}$.

Similar substances have been described in other parts of the body; in the present investigation two were separated from pus; these are designated pyosin, $C_{57}H_{110}N_2O_{15}$, or $C_{56}H_{110}N_2O_{15}$, and pyogenin, $C_{68}H_{128}N_2O_{19}$.

The opinion is expressed that these substances and the similar ones in testicular cells are contained in the cytoplasm, not in the nucleus.

W. D. H.

Chemical Constitution of Peptones. By P. Schützenberger (*Compt. rend.*, **115**, 764—768).—Fibrin-peptone, obtained from the blood of the horse in the manner previously described, is evidently not homogeneous. If a somewhat syrupy solution obtained by concentration on a water-bath is mixed with gradually increasing quantities of strong alcohol, precipitates are obtained which are more and more soluble in alcohol. About one-fifth of the fibrin-peptone remains in solution, even when the liquid contains from 85 to 90 per cent. of alcohol. The composition of the various fractions is not identical, but indicates that they are probably different terms in a homologous series. The first precipitate has the composition $C_{79}H_{51}N_8O_{13}$, whilst the mean composition of all the fractions is $C_{31}H_{55}N_8O_{13}$. The portion soluble in alcohol has the composition $C_{30}H_{56}N_8O_{13}$. The various fractions, when heated for four or five hours at 180° with 3 parts of barium hydroxide, all behave like fibrin-peptone and yield ammonia, carbonic anhydride, acetic acid, and a non-volatile residue consisting of a mixture of amido-acids. This residue, in all cases, when dried in a vacuum at the ordinary temperature, has the composition $mC_9H_{18}N_2O_5$; if heated at 100°, it loses water. The similar residue obtained from the fraction soluble in alcohol has the composition $mC_9H_{20}N_2O_5$.

Phosphotungstic acid, free from alkalis, precipitates only about half the fibrin-peptone. The precipitated fraction, when separated from the phosphotungstic acid and dried in a vacuum over sulphuric acid, is a colourless, friable substance, soluble in water but not hygroscopic. It contains oxygen and nitrogen in the ratio of 1·27 : 1, and carbon and hydrogen in the ratio of about 1 : 1·9. When heated with barium hydroxide, it loses about one-fourth of its nitrogen in the form of ammonia and 1 mol. of carbonic anhydride is liberated for

every 2 mols. of ammonia. The residue of amido-acids has the composition $p(C_nH_{2n}N_2O_4)$ or $C_{nn}H_{2nn}NO_2$, n being between 9 and 10 and very near 9.

The portion not precipitated by phosphotungstic acid contains oxygen and nitrogen in the ratio of 2 : 1, and carbon and hydrogen in the ratio of 1 : 1·7. When heated with barium hydroxide, it loses one-fifth of its nitrogen in the form of ammonia. 1 mol. of carbonic anhydride is formed for every 2 mols. of ammonia, and the other products are acetic acid and a residue of amido-acids of the composition $p(C_nH_{2n}N_2O_4)$ where n is again between 9 and 10 and is very near 9.

The portion of the fibrin-peptone soluble in alcohol gives similar results except that it contains C_nH_{2n+2} instead of C_nH_{2n}.

It follows that fibrin-peptone from the horse can be split up into two parts by the action of phosphotungstic acid, one which is precipitated and contains a lower proportion of oxygen, and another which is not precipitated and contains a higher proportion of oxygen. The excess of oxygen in the latter exists in the form of hydroxyl, and the fibrin itself must be regarded as a compound ether hydrolysable by pepsin, yielding two products which are both ureïdes.

C. H. B.

γ-Achroglobin, a New Respiratory Globulin. By A. B. Griffiths (*Compt. rend.*, **115**, 738—739).—The blood of the *Tunicata* (*Ascidia*, *Molgula*, *Cynthia*) contains a third achroglobin which, like those obtained from *Patella* and the *Chitons*, dissolves in alkaline carbonates and phosphates. It has the composition $C_{721}H_{915}N_{194}SO_{233}$, and exists in two states, oxidised and reduced, and may be called *γ-achroglobin*. 100 grams absorb 149 c.c. of oxygen at 0° and 760° mm. It loses its oxygen in a vacuum and the reduced γ-achroglobin combines with methane, carbonic oxide, and acetylene, forming colourless compounds which dissociate in a vacuum. When dissolved in a solution of magnesium sulphate, its specific rotatory power is $[\alpha]_D = -63°$.

It is highly probable that several colourless respiratory substances exist in the blood of invertebrates. C. H. B.

Pigments of Lepidoptera. By A. B. Griffiths (*Compt. rend.*, **115**, 958—959; compare Hopkins, Proc., 1889, 117).—A green pigment is obtained from the wings of butterflies of several genera and species by extracting them with dilute acid, after cleaning them with alcohol and ether. On evaporating the clear extract, the pigment separates.

Lepidopteric acid, $C_{11}H_{12}N_2O_{10}$, is bibasic, dissolves in alkalis, and forms a *disilver salt*, of which the rotatory power in alcoholic solution is $[\alpha]_D = +29°$. By prolonged boiling with water, the acid is split up into carbamide, alloxan, and carbonic anhydride, but on similar treatment with hydrochloric acid, it is converted into carbonic anhydride and uric acid. It is thus probably a derivative of the latter, deposited in the wings by wandering cells, and therefore of excretory nature. Jn. W.

Organic Chemistry.

Californian Petroleum. By F. Lengfeld and E. O'Neill (*Amer. Chem. J.*, **15**, 19—21).—The crude petroleum from Pico Cañon, in the San Fernando Mountains, Los Angelos County, is viscid, and of a dark-green colour. Its sp. gr. is 0·8414 at 15°, and its refractive index is 1·4810 at 14°. When fractionated, it yields oils boiling from below 40° to 306°, and having sp. gr. varying from 0·6344 to 0·8649, and refractive indices varying from 1·3669 to 1·4824. The lower fractions are colourless; the higher are slightly coloured, and have a marked fluorescence. A preliminary examination shows that the oil contains paraffins, naphthenes, and homologues of benzene, and is probably intermediate in character between Pennsylvanian and Russian petroleum. Jn. W.

Some Cases of Isomerism in the C_6 Series. By G. Griner (*Ann. Chim. Phys.* [6], **26**, 305—394.—The author has studied the tetrabromides and dihydriodides of diallyl, and has prepared a number of new unsaturated fatty hydrocarbons and their derivatives; most of the compounds investigated were found to exist in two or more geometrically isomeric forms, the number of which frequently equalled, but in no case exceeded, that of the modifications foreseen by the theory of Le Bel and Van't Hoff. The first part of the paper is devoted to a discussion of the geometrical constitution of the compounds in question.

Diallyl is best prepared by adding allyl iodide (5 parts) in small quantities at a time to a finely divided alloy (6 parts) of tin (4 parts) and sodium (1 part), heated at about 110°; the product is purified by fractional distillation, the yield being more than 95 per cent. of the theoretical.

When diallyl, boiling at 58·5—59·5°, is treated with bromine in chloroform solution at a temperature below −10°, it yields the two tetrabromides, $C_6H_{10}Br_4$, described by Sabanéeff. The one melts at 53—54°, and crystallises in plates which seem to belong to the clinorhombic system, whilst the other melts at 64—65°, and crystallises in orthorhombic prisms; the liquid tetrabromide described by Ciamician and Anderlini is not formed under the conditions employed by the author. The formation of two dibromides from diallyl is in accordance with stereochemical considerations, and is not to be ascribed to the presence of dipropenyl (compare Wagner, Abstr., 1889, 226; 1890, 223), the tetrabromides of which have properties quite different from those of either of the compounds obtained from diallyl; as, moreover, dipropenyl boils above 77°, whereas diallyl boils at 58·5—59·5°, the presence of the former in the preparations employed by the author is highly improbable.

Two stereoisomeric *dihydriododiallyls*, $CHMeI{\cdot}CH_2{\cdot}CH_2{\cdot}CHMeI$, are formed, together with the monhydriodo-compound boiling at

57—58°, under a pressure of 10 mm., described by Wurtz, when anhydrous hydrogen iodide is passed into diallyl cooled to −20°; the one is a crystalline substance melting at 44°, and boiling at 133—134°, under a pressure of 15 mm.; the other does not solidify even at −60°, and boils at 132—133° under a pressure of 15 mm.

Wurtz's monhydriododiallyl has the constitution

$$CHIMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2,$$

and boils at 163—165°, with slight decomposition, under the ordinary atmospheric pressure; on treatment with boiling concentrated alcoholic potash, it yields an oil boiling at 64—72°, which is a mixture of two stereoisomeric allylpropenyls, $CHMe{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$, and dipropenyl. These compounds cannot be separated by fractional distillation, but their tetrabromides can be isolated. When the crude oil boiling at 64—72° is treated with bromine, it yields besides two crystalline tetrabromides which can be separated with the aid of chloroform, an oily tetrabromide, which does not solidify at −50°, and which is a derivative of allylpropenyl. One of the crystalline products is *dipropenyl tetrabromide*, $CHMeBr{\cdot}CHBr{\cdot}CH{\cdot}CHMeBr$; it forms flat prisms melting at 182—183°. The second crystalline product is *allylpropenyl tetrabromide*; it forms small plates melting at 63—64°.

A mobile oil, boiling at 77—88°, which probably contains three stereoisomeric *dipropenyls*, $CHMe{:}CH{\cdot}CH{:}CHMe$, and a little *allylpropenyl*, is formed when the crystalline dihydriododiallyl referred to above is treated with concentrated alcoholic potash; the several products cannot be separated by fractional distillation. When the oily mixture is treated with bromine, it gives (*a*) a tetrabromide, $C_6H_{10}Br_4$, melting at 182—183°, identical with the dipropenyl derivative just mentioned; (*b*) a tetrabromide, $C_6H_{10}Br_4$, which crystallises in small prisms melting at 95—97°; (*c*) a tetrabromide, $C_6H_{10}Br_4$, which forms large, clinorhombic plates, and melts at 64—65°; (*d*) a liquid isomeride. The three crystalline tetrabromides yield one and the same hydrocarbon, namely, dimethyldiacetylene (see below), on treatment with alcoholic potash; they are therefore geometrical isomerides of the constitution $CHMeBr{\cdot}CHBr{\cdot}CHBr{\cdot}CHMeBr$, and the hydrocarbon, dipropenyl, from which they are derived, is probably a mixture of three stereochemical isomerides, all of which have the constitution $CHMe{:}CH{\cdot}CH{:}CHMe$. The liquid tetrabromide just referred to gives allenylallylene (see below) and dimethyldiacetylene on treatment with alcoholic potash; the latter is doubtless derived from small quantities of the crystalline tetrabromides, the allenylallylene being probably formed from the liquid tetrabromide of allylpropenyl.

When the crystalline dihydriododiallyl is boiled for a long time with alcoholic potash, an oily tetrabromide is not formed on subsequently treating the product with bromine, because the allylpropenyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CHMe$, as was proved by other experiments undergoes intramolecular change into dipropenyl during the first process; this fact, taken in conjunction with the observations of Favorsky (*Bull. Soc. Chim.*, **65**, 247) on the intramolecular change undergone by acetylenic hydrocarbons, seems to indicate that when such a change

does occur the molecule becomes more symmetrical, and methy groups are formed at the end of the chain.

Diallyl does not undergo intramolecular change, even when heated with alcoholic potash at 150°, its stability being probably due to the symmetry of its molecule.

When the liquid dihydriododiallyl (see above) is treated with alcoholic potash, it yields an oil boiling at 77—84°, from which tetrabromides identical with those of dipropenyl and of allylpropenyl are obtained; it must, therefore, be regarded as a stereochemical isomeride of the crystalline compound, a view which is in accordance with theoretical considerations.

The oil obtained on treating either of the diallyl tetrabromides with alcoholic potash can be separated by fractional distillation into a portion boiling at 83—88°, consisting of hydrocarbons, a portion boiling at 130—155°, consisting of bromallylallylenes of the constitution $CHBr{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$ and $CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$, and intermediate fractions which are mixtures of hydrocarbons and bromo-derivatives.

The fraction boiling at 83—88° partially solidifies at −60°, and consists of dipropargyl, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$, and a liquid which does not solidify at −50°, which is in all probability a mixture of dipropargyl and allenylallylene (see below).

Dipropargyl melts at −6, boils at 86—87°, and has a sp. gr. 0·8191 at 0°; it is a colourless, mobile liquid, and gives with an alcoholic solution of silver nitrate a compound of the composition $C_6H_4Ag_2,2AgNO_3$. When heated at about 100° with alcoholic potash, it first undergoes intramolecular change into allenylallylene, but after some hours it is entirely polymerised.

Allenylallylene, $CMe{:}C{\cdot}CH_2{\cdot}C{:}CH$, is obtained when the liquid allylpropenyl tetrabromide (see above) is treated with alcoholic potash. It is a colourless liquid of sp. gr. 0·8250 at 0°, does not solidify at −60°, and boils at 78—83°; it gradually becomes thick when kept, and is rapidly polymerised by alcoholic potash at 100° without formation of dimethyldiacetylene; it combines with silver nitrate in alcoholic solution, yielding a compound of the composition $C_6H_5Ag,AgNO_3$.

Dimethyldiacetylene, $CMe{:}C\ C{:}CMe$, is formed, as already stated, by the action of alcoholic potash on dipropenyl tetrabromide; it can also be obtained by treating propylene with an ammoniacal solution of cuprous chloride and oxidising the product with potassium ferricyanide; the yield is 50 per cent. of the theoretical, assuming that the copper compound has the composition $(C_5H_3)_2Cu_2$. It sublimes very readily in small prisms, melts at 64°, boils at 129—130°, and is specifically lighter than water; it dissolves freely in ether, alcohol, &c., but is almost insoluble in water. It is remarkably stable, and does not explode on percussion; it does not give a precipitate with an ammoniacal solution of cuprous chloride or with the other acetylenic reagents.

The *tetrabromide*, $CMeBr{:}CBr{\cdot}CBr{:}CMeBr$, prepared by treating the hydrocarbon with a chloroform solution of bromine at a temperature below 0° until a permanent coloration is produced, is a crystalline compound melting at 48°, and readily soluble in the ordinary organic

solvents; on treatment with alcoholic potash, or with sodium amalgam, it is reconverted into the original hydrocarbon; no other tetrabromide seems to be formed from dimethyldiacetylene, a result which is in harmony with stereochemical considerations.

An oil boiling at 143—152°, which consists of ketones of the composition C_6H_8O and diketones of the composition $C_6H_{10}O_2$, is formed when finely-divided dimethyldiacetylene is dissolved in well-cooled concentrated sulphuric acid, and the solution poured on to ice; on treating the oil with potash, only the diketones pass into solution. The portion of the oil which is insoluble in potash is a yellowish liquid of sp. gr. 0·9137 at 0°, and boils at 149—150°; it combines with phenylhydrazine and with bromine at the ordinary temperature, and doubtless consists of the ketone $COMe\cdot CH_2\cdot C{:}CMe$, mixed possibly with a small quantity of the isomeride $COEt\cdot C{:}CMe$. The portion of the oil which is soluble in potash is free from acetonylacetone, $CH_2Ac\cdot CH_2Ac$, and consists of acetylpropionylmethane, $COEt\cdot CH_2Ac$, mixed possibly with dipropionyl, $COEt\cdot COEt$; on treatment with copper acetate, it yields a copper derivative which crystallises in small, violet prisms melting at 197—198° (see below).

When dimethyldiacetylene is heated at 100° with a dilute alcoholic solution of mercuric chloride, it gradually passes into solution, and, on subsequent distillation, an oil boiling at about 145° is obtained; the alcoholic solution of this oil gives, with a saturated solution of copper acetate, a compound of the composition $C_{12}H_{18}O_4Cu$, which melts at 197—198°, and is identical with the copper derivative of acetylpropionylmethane described by Claisen.

A compound of the composition $C_9H_{12}O$ is formed when dimethyldiacetylene is heated with alcoholic potash at 130°; it is a yellowish liquid of sp. gr. 0·8956 at 0°, has a pleasant ethereal odour, and boils at 169—170° under the ordinary pressure, and at 72—73° under a pressure of 20 mm.; determinations of its vapour density gave results agreeing with those required by a compound of the molecular formula $C_9H_{12}O$, so that the compound is formed by the combination of the hydrocarbon with alcohol.

The heat of combustion of dimethyldiacetylene is 847,384 cal., that of dipropargyl being 853,600 cal., and that of benzene 776,000 cal.

Divinyl glycol, $CH_2{:}CH\cdot CH(OH)\cdot CH(OH)\cdot CH{:}CH_2$, is obtained, together with other products, when acraldehyde is submitted to the action of a zinc-copper couple in well-cooled, dilute acetic acid solution; it is a colourless oil of sp. gr. 1·0169 at 0°, and boils at 101—102° under a pressure of 10 mm., and at 197—198° under the ordinary atmospheric pressure, apparently without decomposition. It has a bitter taste and a sweet smell, oxidises on exposure to the air, and does not solidify at −60°; it is miscible with water, alcohol, ether, and chloroform in all proportions. The *diacetyl* derivative, $C_{10}H_{14}O_4$, prepared by heating the glycol with acetic anhydride at 150°, is a colourless liquid of sp. gr. 1·0510 at 0°, and boils at 128—129°, under a pressure of 40 mm.; it is insoluble in water, and when heated with alcoholic barium hydroxide it is reconverted into the glycol. Although divinyl glycol contains two asymmetric carbon

atoms, and can, therefore, exist in different geometrical modifications, the glycol obtained in the manner described seems to be the pure inactive compound, free from the racemic modification; the oil recovered from a 1 per cent. solution in which fungi have been cultivated, is optically inactive and identical with the original preparation.

Three *tetrabromides* of the composition $C_6H_{10}Br_4O_2$ are obtained on treating divinyl glycol with bromine in chloroform solution at −15°. One of these crystallises from boiling benzene in acicular prisms, melts at 174°, is only sparingly soluble in boiling benzene, and is stable at 100°; the second isomeride crystallises from cold benzene, in which it is readily soluble, in silky tufts of needles, melts at 98—99°, and decomposes below 100° with evolution of hydrogen bromide. The third isomeride is an oil, possibly a mixture.

When either of the crystalline tetrabromides just referred to is dissolved in ether, and finely-divided potash added to the warm solution, a crystalline compound of the composition $C_6H_8Br_2O_2$ is formed, together with a liquid, which is a mixture of various isomerides, and boils at 130—165° under a pressure of 20 mm.; the former crystallises in needles or plates, and melts at 102°.

The *tetrabromide*, $C_{10}H_{14}O_4Br_4$, prepared by treating the diacetyl derivative of divinyl glycol with bromine in well-cooled chloroform solution, is a crystalline substance melting at 195—205°; it is possibly a mixture of geometrical isomerides.

A crystalline compound of the composition $C_6H_8(OH)_4Cl_2$ is obtained, together with a large quantity of oily products, when divinyl glycol is treated with hypochlorous acid in the cold; it separates from boiling water in elongated rhombohedra, optically uniaxial and negative, and melts at 204—206° with evolution of hydrogen chloride. It is not identical with the mannitol dichlorohydrin prepared by Bouchardat (*Ann. Chim. Phys.*, **6**, 114); its *tetracetyl* derivative, $C_{14}H_{20}O_8Cl_2$, melts at 169—170°, that of mannitol dichlorohydrin at 128—130°.

The *dibromide*, $CH_2{:}CH{\cdot}CHBr{\cdot}CHBr{\cdot}CH{:}CH_2$, can be obtained by dissolving divinyl glycol in well-cooled phosphorus tribromide; it crystallises from ether in triclinic prisms, and melts at 84·5—85°. It combines readily with bromine in well-cooled chloroform solution, yielding a small quantity of a *tetrabromide*, $C_6H_8Br_4$, which crystallises in prisms melting at 112°, and a much larger quantity of an *isomeride*, which crystallises in prisms melting at 105—109°; these two tetrabromides are also formed when divinyl glycol is poured on to well-cooled phosphorus pentabromide.

The compound $CH_2{:}CH{\cdot}CH(OEt){\cdot}CH(OEt){\cdot}CH{:}CH_2$ is formed, and not the hydrocarbon $CH_2{:}CH{\cdot}C{:}C{\cdot}CH{:}CH_2$, as might have been expected, when the dibromide of divinyl glycol is heated with concentrated alcoholic potash; it is a colourless, sweet-smelling liquid of sp. gr. 0·9110 at 0°, and boils at 111—113° under a pressure of 10 mm., and at 224—226° under the ordinary atmospheric pressure; it combines with bromine with great energy.

The tetrabromides melting at 112° and 108—109° respectively give with alcoholic potash a hydrocarbon which has doubtless the consti-

tution $CH_2{:}CH{\cdot}C{:}C{\cdot}C{:}CH$; it gives a precipitate with an ammoniacal solution of cuprous chloride and a yellow precipitate with an alcoholic solution of silver nitrate. F. S. K.

Decomposition of Chloroform in presence of Iodine. By A. Besson (*Compt. rend.*, **116**, 102—103).—Iodine facilitates the decomposition of chloroform by heat. If two tubes, one containing pure chloroform and the other chloroform mixed with a small quantity of iodine, are heated at 250—275° for the same time, the first shows no signs of change, but the second contains carbon, and when opened gives off small quantities of hydrogen chloride and a carbon chloride.

If chloroform vapour containing 1 per cent. of iodine is passed through a tube containing pumice stone heated to incipient redness, the crude product, after separation of unaltered chloroform, has the following composition: carbon dichloride, C_2Cl_4, 35 per cent.; carbon hexachloride, C_2Cl_6, 20 per cent.; carbon tetrachloride, CCl_4, 15 per cent.; hexachlorobenzene, C_6Cl_6, 10 per cent.; carbon sesquichloride, C_4Cl_8, 8 per cent., and other products containing a small quantity of the compound C_2HCl_5 and small quantities of iodine compounds. The precise composition of the product depends on the temperature at which decomposition has taken place. C. H. B.

Synthesis of Mononitroparaffins. By I. Bewad (*Ber.*, **26**, 129—139; compare Abstr., 1891, 653).—When chloropicrin is treated with zinc ethide, the following reactions take place:—(1) $CCl_3{\cdot}NO_2 + 3ZnEt_2 = CEt_3{\cdot}NO_2 + 3ZnEtCl$; (2) $CCl_3{\cdot}NO_2 + 3ZnEt_2 = CHEt_2{\cdot}NO_2 + 3ZnEtCl + C_2H_4$; (3) $CCl_3{\cdot}NO_2 + 3ZnEt_2 = CH_2Et{\cdot}NO_2 + 3ZnEtCl + 2C_2H_4$; (4) $CCl_3{\cdot}NO_2 + 3ZnEt_2 = CH_3{\cdot}NO_2 + 3ZnEtCl + 3C_2H_4$. Zinc methide acts on halogen nitroparaffins in a similar manner, except that it does not bring about the formation of an unsaturated hydrocarbon; in the case of bromonitropropane, for example, the following equations express the various actions:—(1) $CMe_2Br{\cdot}NO_2 + ZnMe_2 = CMe_3{\cdot}NO_2 + ZnMeBr$; (2) $CMe_2Br{\cdot}NO_2 + ZnMe_2 = CMe_3(ZnMe){\cdot}NO_2 + MeBr$. The zinc compound formed in the latter case is decomposed on treatment with water with evolution of methane:—$CMe_2(ZnMe){\cdot}NO_2 + 2H_2O = CHMe_2{\cdot}NO_2 + Zn(OH)_2 + CH_4$. Since the above reactions occur in the case of other simple bromo- and chloro-nitroparaffins, the synthesis of the higher nitroparaffins can be readily accomplished. For this purpose, the zinc alkyl derivative and some dry ether are placed in a flask filled with carbonic anhydride and cooled with ice cold water, and the halogen nitrocompound, or its ethereal solution, gradually added; after keeping for a few days, first in the cold and then at the ordinary temperature, the mixture is carefully treated with water, the products distilled with steam, the distillate acidified with hydrochloric acid, and the ethereal solution separated; the several compounds are separated by the aid of potash or by fractional distillation, or by a combination of these two processes.

Secondary nitropropane, $CHMe_2{\cdot}NO_2$, prepared from bromonitroethane and zinc methide, is a liquid of sp. gr. 1·024 at 0°, and boils at

117—120°. On reduction with zinc and sulphuric acid, it is converted into an amine, the platinochloride of which has the composition $(NH_2Pr^{\beta})_2,H_2PtCl_6$. The identity of the nitropropane with the compound prepared by V. Meyer's method was proved by converting it into propylpseudonitrol, melting at 76°. The bromo-derivative, $CBrMe_2{\cdot}NO_2$, is a neutral oil of sp. gr. 1·6562 at 0°, and boils at 151—153° under a pressure of 712 mm.

Secondary nitrobutane, $CHMeEt{\cdot}NO_2$, is formed, together with nitroethane, when bromonitroethane is treated with zinc ethide; it is a liquid of sp. gr. 0·9877 and boils at 138—139° under a pressure of 747 mm.; it can be converted into butylpseudonitrol, melting at 58°, and into an amine, the platinochloride of which has the composition $(C_4H_9{\cdot}NH_2)_2,H_2PtCl_6$.

Tertiary nitrobutane, $CMe_3{\cdot}NO_2$, can be prepared by treating bromonitropropane, dibromonitroethane, or chloropicrin with zinc methide; when dibromonitroethane is employed, secondary nitropropane and nitroethane are also formed. The properties of this substance have been described (*loc. cit.*).

Tertiary *nitropentane*, $CMe_2Et{\cdot}NO_2$, is formed, together with ethylene and secondary nitropropane, when secondary bromonitropropane is treated with zinc ethide; it is also produced when secondary bromonitrobutane is treated with zinc methide, being accompanied in this case by secondary nitrobutane. It is a colourless, mobile liquid of sp. gr. 0·9783 at 0°, and boils at 149—151° under a pressure of 748 mm.; on reduction with tin and hydrochloric acid, it is converted into an *amine*, the *platinochloride* of which has the composition

$$(C_5H_{11}{\cdot}NH_2)_2,H_2PtCl_6.$$

Tertiary *nitrohexane*, $CMeEt_2{\cdot}NO_2$, is formed, together with secondary nitrobutane and nitroethane, by the action of dibromonitroethane on zinc ethide; it is a colourless liquid of sp. gr. 0·9775 at 0°, and boils at 170—172° under a pressure of 749 mm.; it is insoluble in alkalis, and does not react with bromine or with nitrous acid.

Tertiary *nitroheptane*, $CEt_3{\cdot}NO_2$, secondary nitropentane, primary nitropropane, and nitromethane are produced by the action of zinc ethide on chloropicrin. The tertiary nitroheptane was not obtained in a pure condition; the impure substance is insoluble in potash, does not react with bromine or with nitrous acid, and on reduction is converted into a base, the *platinochloride* of which has the composition $(C_7H_{15}{\cdot}NH_2)_2,H_2PtCl_6$. Secondary *nitropentane*, $CHEt_2{\cdot}NO_2$, is a colourless, mobile, pleasant smelling liquid of sp. gr. 0·9757 at 0°, and boils at 152—155° under a pressure of 746 mm.; it forms a sodium derivative which is only very sparingly soluble in alcohol, and its alkaline solution gives with nitrous acid a colourless, crystalline *amylpseudonitrol*, melting at 66° with decomposition; on reduction, it is converted into an *amine*, the *platinochloride* of which has the composition $(C_5H_{11}{\cdot}NH_2)_2,H_2PtCl_6$. The *bromo*-derivative, $C_5H_{10}Br{\cdot}NO_2$, is a yellowish oil of sp. gr. 1·4562; it is insoluble in water and alkalis.

F. S. K.

Methyl and Ethyl Alcohol as Solvents. By C. A. Lobry de Bruyn (*Zeit. physikal. Chem.*, **10**, 782—789; *Rec. Trav. Chim.*, II, 112—157; and *Ber.*, **26**, 268—274).—The author confirms in the first instance the rule given by Dumas and Péligot that methyl alcohol occupies a position as a solvent intermediate between that of water and ethyl alcohol. Exceptions to this rule are offered by hydrogen chloride, mercuric chloride and iodide, the aromatic nitro-compounds, nitroglycerol, and collodion-cotton, which are more soluble in methyl alcohol than in water or ethyl alcohol. A curious and unexpected behaviour was encountered in the case of salts containing water of crystallisation, and more especially noticeable in the case of sulphates of the dyad metals. These are soluble in methyl alcohol, in some cases to a very considerable extent, but the solutions formed are unstable, and deposit the salt again on standing. The addition of a few drops of water accelerates the deposition, so that the salts are less soluble in methyl alcohol containing water than in methyl alcohol alone. The salt separating from the solution generally contains less water of crystallisation than that originally dissolved, and, in some cases, a replacement of a portion of the water by the alcohol is found to have taken place.

The author points out that methyl alcohol might in many cases be used with advantage in place of ethyl alcohol in the laboratory as a solvent. It does not oxidise so readily, nor is it so susceptible to the action of chlorine, bromine, and iodine. In many cases reagents, such as sodium, potassium cyanide, ammonia, and hydroxylamine, are found to be more soluble in methyl than in ethyl alcohol, and solutions in the former are, therefore, to be preferred to solutions in the latter. H. C.

Pinacone and its Derivatives. By F. Couturier (*Ann. Chim. Phys.* [6], **26**, 433—501).—The following experiments were undertaken with the object of proving or disproving the supposed identity of the chloro-derivatives of pinacone and pinacoline.

When anhydrous pinacone is treated with phosphorus oxychloride, it yields pinacoline and a small quantity of a compound of the constitution $OH\cdot CMe_2\cdot CMe_2Cl$, which is identical with the chlorhydrin obtained by Eltekow (*Ber.*, **16**, 399) by the union of hypochlorous acid with tetramethylethylene.

The dichloro-derivative, $CMe_2Cl\cdot CMe_2Cl$, is formed in small quantity when pinacone is treated with phosphorus trichloride in the cold; it is a crystalline compound, sublimes very readily, melts at 160° when heated in a sealed capillary tube, and is identical with the dichlorodiisopropyl described by Schorlemmer (*Annalen*, **144**, 184). The corresponding *dibromo*-derivative, $C_6H_{12}Br_2$, prepared in like manner, crystallises in long prisms, sublimes readily, and melts at 173—174° with partial decomposition when heated in a sealed tube; it does not react with hydroxylamine, and, when heated with alcoholic potash, it is immediately converted into tetramethylethylene with elimination of 2 atoms of bromine; when heated with water and silver oxide, it yields pinacone, whereas potassium carbonate converts it into a mixture of pinacone and pinacoline.

The *dibromo*-derivative, $CMe_3 \cdot CMeBr_2$, is formed when pinacoline is treated with phosphorus tribromide in the cold; it sublimes readily, and melts at 187° when heated in a sealed tube. The corresponding *dichloro*-derivative, prepared in like manner, is reconverted into pinacoline when heated with water at 100°; it reacts with hydroxylamine, yielding a crystalline *oxime*, $CMe_3 \cdot CMe{:}NOH$, which melts at 74°.

Diacetylpinacone, $C_6H_{12}(OAc)_2$, is formed when pinacone is mixed with acetic anhydride, and the mixture kept for a long time at the ordinary temperature; it is a colourless, crystalline compound, and melts at 65°. When pinacone is heated at 90—95° with acetic anhydride, it is converted into β-dipropylene (Abstr., 1891, 282) and other products, only a very small quantity of the diacetyl derivative being formed.

The alcohol of the composition $C_6H_{14}O$, obtained by reducing pinacoline, combines with acetic acid forming an acetate; from the results of determinations of the initial velocity and limit of etherification, it would seem that the compound in question is a secondary alcohol, a view which is supported by the fact that not a trace of an unsaturated hydrocarbon is formed during the process.

Pinacolyl chloride, $CMe_3 \cdot CHMeCl$, prepared by treating the alcohol just referred to with hydrogen chloride, undergoes complete dissociation at 100° into hydrogen chloride and hydrocarbon, combination taking place again on cooling. The corresponding *bromide*, $CMe_3 \cdot CHMeBr$, melts at 24—25°, and boils at 132° with partial decomposition under a pressure of 758 mm.; it undergoes partial dissociation at 100°, but even at 183° the process is not complete. β-Hexyl chloride does not dissociate at 130°.

Pseudobutylethylene, $CMe_3 \cdot CH{:}CH_2$, is formed, together with tetramethylethylene, when pinacolyl bromide is heated with finely divided potash; it is a colourless liquid of sp. gr. 0·6795 at 0°, boils at 56—58°, and combines with bromine, yielding a liquid *dibromide*, $C_6H_{12}Br_2$, which does not solidify at −23°.

Pseudobutylethylene glycol, $CMe_3 \cdot CH(OH) \cdot CH_2 \cdot OH$, prepared by oxidising the hydrocarbon with potassium permanganate, is a colourless, viscous liquid of sp. gr. 0·9986 at 0°; it boils at 197° under a pressure of 755 mm., and is miscible with water and ether in all proportions. The *diacetyl* derivative, $C_6H_{12}(OAc)_2$, boils at 217—218° under a pressure of 760 mm.

Tetramethylethylene is readily oxidised by potassium permanganate yielding pinacone; the formation of tetramethylethylene from pinacolyl bromide by the action of potash is, doubtless, the result of intramolecular change; aqueous ammonia at 100° converts pinacolyl bromide into tetramethylethylene only, so that this reaction can be conveniently employed for the preparation of the pure hydrocarbon.

β-Dipropylene (*loc. cit.*) is converted into pinacoline when heated with very dilute sulphuric acid at 100°; it combines with nitric peroxide in ethereal solution, yielding a compound of the composition $C_6H_{10}(NO_2)_2$, which crystallises in colourless needles melting at 72—73°.

The pinacone, $C_{12}H_{26}O_2$, which is obtained as a bye-product in the

reduction of pinacoline, is decomposed by dilute sulphuric acid into tetramethylethylene and pinacoline. F. S. K.

Bye-products of the Action of Sodium Hydroxide on Glycerol. By L. Raisonnier (*Bull. Soc. Chim.* [3], **7**, 554).—In the preparation of propylene glycol by the action of soda on glycerol, Fernbach (Abstr., 1881, 145) obtained as bye-products, methyl, ethyl, and propyl alcohols. The author has recognised the presence of the first two, but has not succeeded in isolating propyl alcohol from the bye-product; he has, however, separated a small quantity of allyl alcohol. A. R. L.

Supposed Secondary Hexyl Alcohol from Mannitol. By A. Combes and Le Bel (*Bull. Soc. Chim.* [3], **7**, 551—552).—Erlenmeyer succeeded in converting hexyl iodide from mannitol into an alcohol which, from a study of its decomposition products, he supposed to be a secondary alcohol. When a 0·5 per cent. solution of this alcohol is submitted to the action of *Penicillium glaucum*, the solution, on concentration, was found to be dextrorotatory. Now this result is surprising, inasmuch as it has been shown by one of the authors that methylpropylcarbinol and methylethylcarbinol give lævorotatory solutions after the action of *Penicillium glaucum*.

The authors next prepared methylbutylcarbinol by the hydrogenation of methyl butyl ketone, obtained by decomposing propylacetylacetone, COMe·CHPr·COMe, with potash. By cultivating *Penicillium glaucum* in a solution of the alcohol so prepared, a lævorotatory liquid was obtained, as might have been expected.

Finally, ethylpropylcarbinol was prepared by distilling a mixture of calcium butyrate and propionate, and hydrogenising the resulting ethyl propyl ketone. A solution of this alcohol, like one of that prepared from mannitol, became dextrorotatory after cultivating *Penicillium glaucum* in it, so that there can be no doubt that the alcohol from mannitol is ethylbutylcarbinol. The chloride derived from the last-named alcohol is lævorotatory, and the iodide is dextrorotatory in accordance with Guye's theory. A. R. L.

Pentacetyl Derivatives of Glucose (Dextrose). By A. P. N. Franchimont (*Rec. Trav. Chim.*, **11**, 106—111).—The compound of melting point 134°, obtained by heating a mixture of glucose and sodium acetate with acetic anhydride, is a pentacetylglucose, and not an octacetyldiglucose, as stated by Herzfeld and by Erwig and Königs; it is optically inactive. The author confirms Erwig and König's observation (Abstr., 1889, 952) that a pentacetylglucose, melting at 112°, is produced by heating glucose with acetic anhydride and zinc chloride; it is much more soluble in water and alcohol than the first-mentioned isomeride, besides which it is feebly dextrorotatory. Both compounds yield glucose on hydrolysis with aqueous ammonia, and the author hopes later to be able to explain their isomerism. He suggests that the decacetyldiglucoheptose obtained by Fischer (Abstr., 1892, 1167) may turn out to be a hexacetylglucoheptose. Fischer's analytical values agree equally well with those

demanded for the last-named compound, and he did not make an acetyl determination. A. R. L.

Chloralose, a Derivative of Chloral, and its Physiological Properties. By HANRIOT and C. RICHET (*Compt. rend.*, **116**, 63—65).—Equal quantities of anhydrous chloral and dry glucose are heated together at 100° for an hour, and the cooled product is mixed with a small quantity of water and extracted with boiling ether. The portion soluble in ether is distilled repeatedly with water until all chloral is expelled, and the aqueous solution is then subjected to fractional crystallisation; in this way, the anhydroglucochloral which has already been described by Heffter (Abstr., 1889, 845), and which the authors propose to call *chloralose*, is obtained in two forms, namely, chloralose, which crystallises in slender needles melting at 184—186°, and volatilising without decomposition, and *parachloralose*, which crystallises in nacreous lamellæ melting at 229°. The latter is soluble with difficulty even in hot water. Both substances have the composition $C_8H_{11}Cl_3O_6$.

Chloralose with sulphuric acid yields a disulphonic derivative, and with acetic anhydride a tetracetyl derivative. Contrary to the statement of Heffter, it does not yield glucose when treated with potassium hydroxide.

Parachloralose, probably by reason of its insolubility, is without physiological activity, but chloralose, when administered by ingestion, produces hypnotic effects, and at the same time increases the excitability of the spinal marrow. When given to dogs in the proportion of 0·6 gram per kilogram of body weight, it produces only anæsthæsia, and not death. The hypnotic effect begins to be evident with doses so small as 0·02 gram per kilogram of body weight, and hence chloralose is much more active than chloral, and its effect cannot be attributed to a decomposition into chloral. When administered to human beings in doses of from 0·2 gram to 0·75 gram, but not exceeding 1 gram, it acts as a valuable hypnotic, producing no disturbance of digestion, no cephalalgia, and no phenomena of intoxication. C. H. B.

Soluble Pentoses in Plants. By G. DE CHALMOT (*Amer. Chem. J.*, **15**, 21—38).—The same reasoning which tends to show that hexoses in plants are built up in the leaves from formaldehyde also holds good for pentoses, and it is probable that the pentosans found in other parts of the plants as constituents of the cell-walls are formed from pentoses in the places where they are found. Hence these pentoses must be soluble. To test this, the leaves of a large number of plants representative of most classes and orders were extracted with water, the extract, after purification with lead acetate, distilled with 12 per cent. hydrochloric acid, and the distillate tested with aniline acetate for furfuraldehyde. The latter was found in every case, although in some cases in very small quantity. To determine whether an amount of furfuraldehyde sufficient to mask these results would be yielded by hexoses under this treatment, the furfuraldehyde obtained both from the leaves and from a known quantity

of invert sugar was estimated by a colorimetric method based on the formation of the red dye $2NH_2Ph,C_5H_4O,HCl,H_2O$ when aniline and furfuraldehyde are added to alcoholic acetic acid. The result showed that invert sugar yields only 0·2 per cent. of furfuraldehyde, which, calculated on the hexoses present, in trefoil for instance (0·89 per cent.), would correspond with only 0·002 per cent. of furfuraldehyde from the trefoil, which actually yielded, however, 0 1 per cent. In all cases similar results were obtained, and the quantity of hexoses present was insufficient to account for the formation of the furfuraldehyde, which presumably, therefore, arose from soluble pentoses.

The actual amount (at the most 0·5 per cent.) of these pentoses in the leaves and colourless bark of plants is small compared with that of the hexoses, of which as much as 1·8 per cent. may be present. The pentoses readily diffuse through membranes, and are therefore presumably simple sugars of the composition $C_5H_{10}O_5$.

In many plants, a larger quantity of pentoses is present in the evening than in the morning, so that, like the hexoses, they are probably converted into temporary solid forms immediately after their formation.

Jn. W.

Xylose. By G. Bertrand (*Bull. Soc. Chim.* [3], **7**, 499—502).—Xylose occupies an important place in the vegetable kingdom, since it is invariably found amongst the decomposition products of the incrusting substances of the angiosperms. It frequently crystallises in prisms, belonging to the orthorhombic system, which polarise light. 100 parts of water at 20·3° dissolve 117·05° parts of xylose; it is insoluble in absolute alcohol, but 10 c.c. of a solution in 90 per cent. alcohol, saturated at 19°, were found to contain 0·3–9 gram of the sugar. The rotatory power in a solution approximating 10 per cent. concentration was found to be $[\alpha]_D = +19·4°$ at 23° (compare Wheeler and Tollens, *Annalen*, **254**, 309; Hébert, Abstr., 1890, 1460). Xylose is not fermentable with yeast, and its cupric reducing power (Fehling's solution) is 109·6 per cent. that of glucose, or 104 per cent. that of invert sugar. When either xylose or arabinose is gently heated with a small quantity of hydrochloric acid, furfuraldehyde is produced which gives, on addition of a little orcinol, a violet-blue coloration; under the same conditions, the hexoses give an orange-red coloration. When xylose is allowed to remain for 24 hours in contact with 30—50 times its weight of bromine water, the excess of bromine expelled by boiling, and cadmium carbonate added, the addition of an equal volume of alcohol to the concentrated filtrate gives a *compound*, $C_5H_9O_5{\cdot}CdBr + H_2O$, which crystallises in prismatic needles, and has no melting point, but swells up when heated: the formation of this compound is characteristic of xylose.

A. R. L.

Sugar from Pear Pectose. By R. W. Bauer (*Landw. Versuchs-Stat.*, **41**, 477).—Pear pectose (5 grams, containing 4·731 grams of dry matter), when boiled with 2 per cent. sulphuric acid for four hours, gave a filtrate which polarised +12° with 100 mm. The solution was made up to 200 c.c. with absolute alcohol, and neutralised with calcium carbonate. The solution polarised +2°; it contained 0·5955 gram of sugar crystals and optically active gum. This

gave, with phenylhydrazine, an osazone crystallising in stellate groups of microscopic needles melting at 195°. The needles are pleochroic, and give a slightly dextrorotatory solution in glacial acetic acid. The compound is, therefore, probably galactosazone.

N. H. M.

Inversion of some Carbohydrates. By E. WINTERSTEIN (*Landw. Versuchs-Stat.*, **41**, 375—384).—The object of the experiments, which were made with stachyose and with lupeose (β-galactan), was to ascertain the amount of acid and the length of time necessary to bring about complete inversion; also to determine the amounts of glucose formed. Determinations were also made with raffinose, wood-gum (from beech-wood meal; Wheeler and Tollens), and with cellulose (pure cotton wool extracted with 0·5 per cent. aqueous soda, and a preparation from lupin hulls).

The substance, dried at 105—110°, was boiled with a known volume of dilute sulphuric acid, the whole made up to a definite bulk, and the glucose determined in a portion by Allihn's method. The results are calculated as if dextrose alone were present, using Allihn's grape sugar tables. The error is only slight, as the reducing power of the known glucoses does not differ much.

With stachyose, the best results, 74·52 per cent. of the theoretical amount, were got by boiling for one hour with 2 per cent. hydrochloric acid; with lupeose, under the same conditions, 78·63 per cent. was obtained. In the case of raffinose, one hour's heating with N/5 hydrochloric acid gave the highest yield (86·78 per cent.). Wood-gum gave the highest percentage (77·92) when boiled with 2 per cent. acid for one hour.

Cotton-wool cellulose (0·9668 gram dry and free from ash) was treated with concentrated sulphuric acid (5 grams) and, after 12 hours, diluted with water, filtered, and diluted to 200 c.c. This was boiled for two hours in a reflux apparatus. 92·40 per cent. of the theoretical amount was obtained. Lupin-hull cellulose treated in the same way gave 93·81 per cent. Longer boiling gave rather lower results.

N. H. M.

Preparation and Purification of the Propylamines. By F. CHANCEL (*Bull. Soc. Chim.* [3], **7**, 405—407).—A mixture of propylamine (45 parts), dipropylamine (35 parts), and tripropylamine (20 parts) is obtained by heating propyl chloride and aqueous ammonia (equal mols.) dissolved in alcohol for 10 hours at 100—110°, in a closed vessel. The three bases are separated by fractional distillation, and are then purified as follows:—Propylamine is converted into dipropyloxamide by treatment with ethyl oxalate; propylamine picrate melts at 135°. Dipropylamine is converted into dipropyloxamic acid by means of oxalic acid. Tripropylamine is purified by crystallising its picrate.

A. R. L.

Thionyldiethylhydrazone. By A. MICHAELIS and O. STORBECK (*Ber.*, **26**, 310—311).—*Thionyldiethylhydrazone*, $NEt_2{\cdot}N{:}SO$, is obtained by adding an ethereal solution of thionyl chloride to an ice-cold ethereal solution of diethylhydrazine. It is a colourless oil, having

a faint aromatic odour, distils undecomposed at 73° under 20 mm. pressure, and is gradually decomposed by water. When treated with sodium hydroxide, it yields hydrazine; with dilute sulphuric acid, it yields sulphurous anhydride. E. C. R.

The Alleged Optical Activity of Chlorofumaric acid. An Active Chlorosuccinic acid. By P. Walden (*Ber.*, **26**, 210—215).—Perkin states (Trans., 1888, 695) that ethyl chlorofumarate and chloromaleate exhibit a slight optical activity (+6')*. This case of optical activity among unsaturated compounds is not easily reconciled with Van't Hoff's hypothesis, according to which such activity is conditioned by the presence of an "asymmetric" carbon atom. The author, therefore, has investigated the matter more closely, and finds that when phosphorus pentachloride is allowed to act on tartaric acid, the temperature never being allowed to rise above 60°, a mixture of chlorofumaric and dichlorosuccinic acids were obtained, but these are both entirely devoid of optical activity.

Another fact which somewhat impairs the generality of Van't Hoff's hypothesis is that, when, in many active compounds, hydroxyl is replaced by a halogen, the resulting substance is inactive. This is not always the case, however, for the author finds that, when phosphorus pentachloride is allowed to act on malic acid at a temperature not exceeding 55°, fumaric acid and a new *dextrorotatory chlorosuccinic acid*, $C_4H_5ClO_4$, are obtained. It is a white substance, has in the mean $[\alpha]_D = +20{\cdot}9°$, and melts at 174° with evolution of hydrogen chloride and formation of fumaric acid. C. F. B.

Electrolysis of Trichloracetic acid. By K. Elbs (*J. pr. Chem.* [2], **47**, 104).—By the electrolysis of an aqueous solution of zinc or sodium trichloracetate, crystals of a compound, which decomposes with evolution of carbonyl chloride and hydrogen chloride, have been obtained. Its properties indicate that it is a derivative of trichloromethyl alcohol; but they do not agree with those of trichloromethyl trichloracetate. A. G. B.

Glycolide and its Homologues. By C. A. Bischoff and P. Walden (*Ber.*, **26**, 262—265).—*Glycolide*, $C_4H_4O_4$, is obtained by the distillation of sodium bromacetate in a vacuum, and crystallises in large, lustrous plates which melt at 86—87°; when heated with water, glycollic acid is formed, whilst with aniline, glycollic anilide is obtained. The yield is 25 per cent. of the salt employed.

The compound hitherto termed glycolide is a polymeride of the preceding substance, and is formed from it by heating it alone or with a trace of zinc chloride; on distillation in a vacuum, glycolide is regenerated. Sodium chloracetate behaves like the bromoacetate.

By the distillation of sodium bromopropionate, either in a vacuum or under the ordinary pressure, the corresponding lactide is obtained.

* The author seems to have consulted the *Jahresbericht*, not the original paper, in which Perkin says (p. 701), "It is difficult to say whether this rotation is due to the pure ether or not, but it appears to be so." [Editors.]

The lactide of hydroxybutyric acid, $\begin{matrix}CO-O-CHEt\\ |\\ CHEt\cdot O\cdot CO\end{matrix}$, together with a little crotonic acid, is obtained in a similar manner from sodium α-bromobutyrate; it boils at 257—258° under a pressure of 760 mm., melts at 21—22°, and has a sweet taste.

On distillation, sodium α-bromisobutyrate yields α-hydroxyisobutyric acid, methylacrylic acid, and its polymeric modification.

The authors consider that the above results tend to confirm the dynamic hypothesis, since they have failed to obtain closed chain compounds containing four methyl groups. J. B. T.

Action of Potassium Permanganate on Organic Acids. By A. Lumière and A. Seyewetz (*Bull. Soc. Chim.* [3], **7**, 538—542). The authors state that potassium permanganate acts in the cold on numerous easily oxidisable organic acids, giving rise to a hydrated manganese dioxide, soluble in an excess of the acid with the production of manganic salts, which latter they propose to study.

When the permanganate is added to oxalic acid in the cold, the following reaction occurs:—$2KMnO_4 + 3H_2C_2O_4 = 2MnO_2,H_2O + K_2CO_3 + 2H_2O + 5CO_2$. In the presence of an excess of the acid, and when the temperature is kept below 30—40°, a brownish-red liquid, which has all the properties of a solution of a manganic salt, is formed; the following equation probably represents the reaction:—$2MnO_2 + 4H_2C_2O_4 = (C_2O_4)_3Mn_2 + 2CO_2 + 4H_2O$. On heating the last-mentioned solution to 60°, or on exposing it to light, it is decolorised, and manganous oxalate separates. The same solution acts as an energetic oxidising agent, and if paper coated with gelatin is impregnated with it, and then plunged into a salt of an amine, colorations which vary according to the nature of the amine are produced. No coloration is produced, however, when the impregnated paper has been exposed to light before treating it with the amine. These properties, which are exhibited also by inorganic manganic salts, have been utillsed by Lumière for a new photographic process (*Bull. Soc. franc. photogr.*, 1892). A. R. L.

Asymmetrical Dicarboxylic acids. By J. W. Brühl and R. Braunschweig (*Ber.*, **26**, 337—345).—In view of the results obtained by the authors in the etherification of camphoric acid (this vol., i, 277), they have examined the behaviour of other asymmetrical dicarboxylic acids under similar conditions, and have selected in the first place pyrotartaric acid (methylsuccinic acid). The *dimethyl* salt, $C_5H_6O_4Me_2$, is obtained in the usual manner, and may be separated from the acid salts simultaneously formed by fractionation in a vacuum, or by treatment with alkalis, which readily hydrolyse the latter substances. It is a colourless liquid, which has a faint pleasant odour, and boils at 197° under 759 mm. pressure, and at 101° under 22 mm. pressure. The *diethyl* salt, $C_5H_6O_4Et_2$, was obtained in a similar manner, and boils at 218° under 759 mm. pressure, and at 125° under 33 mm.

The acid alkyl salts may be obtained by the methods employed in the case of camphoric acid (*loc. cit.*); *orthomethyl pyrotartrate*,

$C_5H_7O_4Me$, is formed by boiling the anhydride with methyl alcohol and is a thick, colourless acid liquid, which is quickly hydrolysed by water, and immediately by alkalis, and boils at 153—153·5° under 20 mm. pressure. The *sodium* salt of the same methyl derivative is obtained by heating together the anhydride and a solution of sodium methoxide in methyl alcohol, or by adding sodium to a solution of the anhydride in methyl alcohol. *Orthoethyl pyrotartrate*, $C_5H_7O_4Et$, is obtained in a similar manner, and forms a colourless, odourless oil, which boils at 160—161° under 22 mm. pressure, and is also hydrolysed with great ease.

An attempt was next made to prepare the "allo-" methyl ether by treating the dimethyl salt with the requisite quantity of potash dissolved in ethyl alcohol, but it was found that, instead of the potassium methyl salt, potassium ethyl pyrotartrate was formed, the methyl group being replaced by the ethyl group in the course of the reaction. The latter compound may also be obtained by the action of alcoholic potash on the diethyl salt, and agrees in its physical properties with the salt obtained from the anhydride and ethyl alcohol; the authors nevertheless do not regard it as impossible that these two compounds are in reality isomeric.

When ethyl orthopyrotartrate is treated with methyl iodide and sodium methoxide in methyl alcohol solution, it is converted into methyl orthoethyl pyrotartrate, $C_5H_6O_4MeEt$, which is a colourless mobile liquid boiling at 101—102° under 20 mm. pressure, and not quite constantly about 198° under 754·1 mm. An attempt to obtain the isomeric orthomethyl ethyl pyrotartrate by the action of ethyl bromide and sodium ethoxide on orthomethyl pyrotartrate in ethyl alcohol solution resulted in the formation of the diethyl salt, the methyl group being in this case also displaced by the ethyl group. A second attempt to prepare it by the action of sodium ethoxide (1 mol.) and ethyl bromide (1 mol.) on a solution of pyrotartaric anhydride in methyl alcohol was likewise unsuccessful, the product being in this case the dimethyl salt.

The spectrometric constants of all the above derivatives were determined, and found to agree closely with the theoretical numbers. Even without the analytical details, the spectrometric investigation was quite sufficient to determine the purity of the compound, and to indicate its nature, even when the action proceeded in an unexpected manner. H. G. C.

Metahydroxyuvitic acid. By H. MEISTER (*Ber.*, **26**, 354—356). —The author has succeeded in preparing the diethyl salt of this acid, $OH{\cdot}C_6H_2Me(COOEt)_2$, in four different ways, and does not find that it is nearly as unstable as stated by Oppenheim and Pfaff (this Journ., 1874, 1161). It crystallises in plates, melts at 45°, boils at 242—243° under 10 mm. pressure, and at 280—310° with partial decomposition at the ordinary pressure; the pure compound crystallises from the distillate even in the latter case.

When treated with the theoretical quantity of sodium or potassium ethoxide, it is converted into the ethyl sodium or ethyl potassium salt, which on boiling with water yields the *monethyl salt*, $C_{11}H_{12}O_5$;

this crystallises in white needles melting at 176—177°, and yields a white, curdy *silver* salt on the addition of silver nitrate.

H. G. C.

Butanetetracarboxylic acid. Synthesis of Pentamethylene Derivatives. By K. Auwers (*Ber.*, **26**, 364—378; compare Abstr., 1891, 546).—By the action of ethyl sodiomalonate on ethyl aconitate in alcoholic solution and subsequent hydrolysis of the product by means of hydrochloric acid, a mixture is obtained consisting of butanetetracarboxylic acid, ketopentamethylenedicarboxylic acid, together with a third acid which melts at 185° with evolution of gas, and is being further investigated. The acids are separated and purified by crystallisation from water.

Butanetetracarboxylic acid melts at 244°, and has been previously prepared by Bischoff from ethyl butanehexacarboxylate; the acid is not affected by potassium permanganate in alkaline solution. The *silver*, *copper*, *lead*, and *barium salts* are sparingly soluble.

The *anhydride*, $O<\begin{matrix}CO\cdot CH—CH\cdot CO\\ CO\cdot CH_2\quad CH_2\cdot CO\end{matrix}>O$, is prepared by the action of acetic chloride on the acid at 100°, and crystallises from acetone, on the addition of light petroleum, in lustrous plates which melt at 172—173°.

Ketopentamethylenedicarboxylic acid, $CO<\begin{matrix}CH_2\cdot CH\cdot COOH\\ CH_2\cdot CH\cdot COOH\end{matrix}$, is deposited in octahedral crystals melting at 189°, and appears to be formed by the elimination of water and carbonic anhydride from butanetetracarboxylic acid; this is analogous to the production of ketopentamethylene from calcium adipate, and of methyl- and dimethyl-ketopentamethylene from β-methyladipic acid and αα-dimethyladipic acid respectively. The *silver*, *lead*, *mercury*, *copper*, *barium*, *calcium*, and *ferric salts* are sparingly soluble. The *dimethyl salt* crystallises from light petroleum in colourless, flat, feathery needles melting at 63—64°. The *diethyl salt* is liquid at ordinary temperatures, and yields an *oxime* which crystallises from dilute alcohol in silky, lustrous, concentric needles melting at 74°. The *phenylhydrazone* of the ethyl salt is deposited from alcohol in yellow needles which melt at 105° and decompose spontaneously.

Ketopentamethylenedicarboxylic acid, when heated at 230—260° under a pressure of 30—40 mm., yields an acid crystallising in slender needles; it melts at 140°, and is being further investigated. By the oxidation of the carboxylic acid with potassium permanganate in alkaline solution, or with nitric acid, oxalic acid is produced.

By the action of ethyl sodioethylenetricarboxylate on ethyl aconitate, and subsequent hydrolysis of the ethereal salt, succinic acid is obtained as the sole product.

J. B. T.

Dipropylcarbamide and Dipropylthiocarbamide. By F. Chancel (*Compt. rend.*, **116**, 62—63).—When propyl isocyanate is added to an aqueous solution of propylamine, there is immediate reaction with considerable development of heat. A mixture of propyl isocyanate and propyl iodide may be used, and the dipropylamine hydr-

iodide that is then formed may be separated from the dipropylcarbamide by washing with cold water, in which it is much the more soluble.

The symmetrical dipropylcarbamide thus obtained, crystallises from hot water in white plates with a micaceous lustre. It melts at 104° and boils at 255°, is very slightly soluble in cold water, and not much more soluble in hot water, but dissolves in alcohol and ether.

Dry propylamine and carbon bisulphide likewise react immediately, with considerable development of heat. If the propylamine (2 mols.) is poured very gradually into the carbon bisulphide (1 mol.) and the mixture is cooled, a readily fusible solid mass is obtained, and if this is heated for about eight hours at 100—110°, hydrogen sulphide is evolved and symmetrical dipropylthiocarbamide is obtained. It is very slightly soluble in cold water, and somewhat more soluble in hot water, from which it crystallises in brilliant lamellæ resembling those of dipropylcarbamide. It melts at 68°, and dissolves readily in alcohol. Concentrated nitric acid completely oxidises dipropylthiocarbamide even at the ordinary temperature. C. H. B.

β-Furfurallevulinic acid; a New Synthesis of Cumarone Derivatives. By E. A. KEHRER and W. KLEBERG (*Ber.*, **26**, 345—353).—The furfurallevulinic acid previously described by Ludwig and Kehrer (Abstr., 1891, 1456) is the δ-derivative and not the β-derivative, as has already been pointed out by Erdmann (Abstr., 1892, 147). β-Furfurallevulinic acid, $C_4OH_3{\cdot}CH{:}CAc{\cdot}CH_2{\cdot}COOH$, may, however, be prepared by heating a mixture of levulinic acid, furfuraldehyde, and anhydrous sodium acetate in molecular proportion in a reflux apparatus. After purification, it crystallises from alcohol in yellow, strongly refractive prisms or tablets, and melts at 153°. It dissolves in concentrated sulphuric acid with a green colour, which on addition of water becomes first greenish-yellow, then yellow, and finally disappears. The *calcium* salt $(C_{10}H_9O_4)_2Ca + 2H_2O$, is a yellow, amorphous compound, and becomes anhydrous at 100°; the *phenylhydrazone*, $C_{16}H_{16}N_2O_3$, crystallises in yellow, rhombic plates, and melts at 168°. As the corresponding β-benzallevulinic acid, when heated, is converted into 3-aceto-1-naphthol with the loss of water, it appeared probable that the β-furfural compound would undergo a similar change with formation of a cumarone derivative, and the authors, therefore, distilled it carefully in a current of hydrogen or carbonic anhydride. The distillate is treated with alkali, and the solution after extraction with ether subjected to the action of a rapid current of carbonic anhydride. The white, flocculent compound, after reprecipitation from alkaline solution, melts at 190°, and has the composition $C_{10}H_8O_3$; it is therefore, in all probability, the expected 3-*aceto*-1-*hydroxycumarone*, its formation corresponding exactly with that of α-naphthol from phenylisocrotonic acid.

In the preparation of δ-furfurallevulinic acid, and also to a lesser extent in the preparation of the β-compound, a yellow, pulverulent substance is obtained, which Erdmann has suggested may be δ-furfural-angelicalactone. The authors find, however, that it is a mixture of furfurallevulinic acid with *βδ-difurfurallevulinic acid*,

$$C_4OH_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C(CH{\cdot}C_4OH_3){\cdot}CH_2{\cdot}COOH.$$

The latter compound melts at 148°, and crystallises from benzene or alcohol in yellow or yellowish-green crystals and from hot water, in which it is very sparingly soluble, in very slender, yellow needles; it reduces Fehling's solution at the boiling point, but not in the cold. When even slight traces of the acid are dissolved in concentrated sulphuric acid, a beautiful, cornflower-blue solution is obtained, which, on careful addition of water, passes through different shades of violet and red to orange and yellow. The reverse series of changes may be observed by gradually adding sulphuric acid to a solution of the acid in absolute methyl or ethyl alcohol. The *calcium* salt, $(C_{15}H_{11}O_5)_2Ca + 3H_2O$, crystallises in bundles of needles, and becomes anhydrous at 100°; the *silver* salt, $C_{15}H_{11}O_5Ag$, is an amorphous precipitate, unaffected by light.

All three acids when reduced with sodium amalgam, yield the corresponding furfuryl derivatives; *δ-furfuryllevulinic acid*,

$$C_4OH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

crystallises in long, transparent needles melting at 98°; *β-furfuryllevulinic acid* in white, granular crystals, or sometimes in needles or prisms melting at 100—101°, and *βδ-difurfuryllevulinic acid* in crystalline groups melting at 71—72°. H. G. C.

Hydro-derivatives of Benzene. By A. Baeyer (*Ber.*, **26**, 229—231). — Hexahydrobenzene is easily prepared by treating quinitol (Abstr., 1892, 833) with hydriodic acid, and reducing the diiodide thus obtained with zinc dust and acetic acid. It is a very volatile oil, having an odour resembling that of petroleum, and is without action on permanganate.

The *iodhydrin of quinitol* is obtained by treating quinitol with dilute hydriodic acid, and is a colourless oil somewhat soluble in water. When treated with alkalis, it yields an oil which has a strong odour of capryl alcohol, is an unsaturated compound, and is probably a tetrahydrophenol.

Hexahydrophenol is easily prepared by reducing the iodhydrin with zinc dust and acetic acid. It boils at 157—159° under 720 mm. pressure, solidifies at a low temperature to a scaly mass, melts at 15°, has an odour resembling that of fusel oil, and is stable towards permanganate in the cold.

Bromhexahydrobenzene is obtained by heating the preceding alcohol with hydrobromic acid. It is a colourless oil, and boils at 162—163° under 714 mm. pressure.

Tetrahydrobenzene is obtained by distilling the preceding monobromide with quinoline. It boils at 82°, and yields a liquid dibromide and a nitrosochloride melting at 152—153°. The alcoholic solution turns yellow on addition of concentrated sulphuric acid.

The dihydrobenzene obtained from the dibromide of quinitol (Abstr., 1892, 1074), when dissolved in alcoholic sulphuric acid, gives a blue solution having a characteristic absorption spectrum with two distinct bands in the yellow and green and a paler one in the blue. It will be of interest to determine if the blue solution of sylvestrene in alcoholic sulphuric acid shows a similar spectrum. Dihydrobenzene and tetrahydrobenzene are easily distinguished.

The former gives a crystalline tetrabromide, and a blue solution with alcoholic sulphuric acid; the latter a liquid dibromide and a yellow solution with alcoholic sulphuric acid.

When the dibromide of tetrahydrobenzene is distilled with quinoline, it yields only a trace of dihydrobenzene; this, however, gives the same absorption spectrum as the dihydrobenzene obtained from quinitol. E. C. R.

Preparation of Orthodinitrobenzene. By C. A. Lobry de Bruyn (*Ber.*, **26**, 266—267).—The residue obtained in the preparation of metadinitrobenzene is heated with 2 parts of commercial nitric acid (sp. gr. 1·4) until the solution is almost colourless, the liquid is then poured into 5—6 parts of cold nitric acid and allowed to remain until the orthodinitrobenzene is deposited; it is then quickly collected, washed with nitric acid, and recrystallised from alcohol.

The author mentions a number of ortho-compounds which may be prepared from pure orthodinitrobenzene. J. B. T.

Reaction of Phenyl Iododichloride and Iodosobenzene. By R. Otto (*Ber.*, **26**, 305—306; compare this vol. i, 149).—Phenyl iododichloride and thiophenol, when mixed in chloroform solution, react energetically with evolution of hydrogen chloride, and yield iodobenzene and phenyl bisulphide.

Phenyl iododichloride and sodium benzenesulphinate, in a similar way, yield benzenesulphochloride and iodobenzene together with a small quantity of a compound melting at 180—190°.

Iodosobenzene reacts with thiophenol in the same way as phenyl iododichloride and yields iodobenzene and phenyl bisulphide.

E. C. R.

Aromatic Iododichlorides, Iodoso- and Iodoxy-compounds. By C. Willgerodt (*Ber.*, **26**, 357—362; compare this vol., p. 149).—Phenyl iododichloride reacts with water at ordinary temperatures forming iodobenzene, hydrochloric acid, hypochlorous acid, and iodosobenzene; the latter compound may be separated by treating the solid product with nitric acid; iodosobenzene is oxidised on evaporating its aqueous solution, iodoxybenzene being formed; this explodes at 230° and at lower temperatures when impure. Iodosobenzene may also be prepared by the action of potash or soda on phenyl iododichloride.

Iodoxybenzene is readily obtained by heating iodosobenzene with water in a retort; iodobenzene volatilises with the steam, and the oxy-compound is deposited on cooling.

Paratolyl iododichloride, $C_6H_4Me{\cdot}ICl_2$, is prepared by the chlorination of pariodotoluene, and is deposited from chloroform in needles which decompose at 85°, whilst from carbon tetrachloride granular, rhombic crystals are formed which explode at 100—118°; with alcohol, it reacts like the corresponding benzene compound.

Pariodosotoluene, $C_6H_4Me{\cdot}IO$, is obtained by the action of soda on the preceding compound, and is purified by treatment with chloroform, which removes iodotoluene; it closely resembles the corresponding

benzene derivative, softens at 130°, and melts, with evolution of gas, at about 175—178°. The *acetate* and *nitrate* are crystalline; the latter decomposes without explosion at 90—92°.

Periodoxytoluene, $C_6H_4Me{\cdot}IO_2$, is prepared in a similar manner to the benzene derivative, and explodes at 228°.

Orthotolyl iododichloride is more readily soluble than the para-compound, and decomposes at about 91° with previous softening.

Orthoiodosotoluene is almost colourless, and decomposes at 178°.

Orthoiodoxytoluene is crystalline, and explodes at 210°.

Parabromiodosobenzene, $C_6H_4Br{\cdot}IO$, is a pale yellow, amorphous compound, decomposing at 185°. The *acetate* and *nitrate* are crystalline; the latter melts at 96—97° with decomposition.

Parabromiodoxybenzene, $C_6H_4Br{\cdot}IO_2$, crystallises from glacial acetic acid in colourless plates, and explodes at 240°. *Paranitroiodosobenzene*, $NO_2{\cdot}C_6H_4{\cdot}IO$, is prepared from paranitrophenyl iododichloride, and decomposes at 78°. J. B. T.

Titanium Compounds. By L. Levy (*Ann. Chim. Phys.* [6], **25**, 433—519).—Most of the work recorded in this paper has been published elsewhere in the course of the last five years (compare Abstr., 1888, 27, 196, 423, 1254; 1889, 572; and 1890, 1066); the following compounds seem not to have been described before.

Phenyl titanate, $Ti(OPh)_4$, prepared by treating titanium tetrachloride with phenol in benzene solution, is a red, crystalline substance, which decomposes at 100°, and melts at about 143° when quickly heated. It is decomposed by nascent hydrogen, yields dichlorophenol on treatment with chlorine, and is converted into tribromophenol and titanium tetrabromide when submitted to the action of bromine vapour; with iodine, it gives iodophenol and titanium tetriodide. It is decomposed by water and by dilute alcohol, yielding phenol and a yellow substance; it dissolves in concentrated mineral acids, and is readily decomposed by alkalis.

A compound of the composition $2TiCl_4,Ti[O{\cdot}C_6H_2(NO_2)_3]_4$ is obtained when titanium tetrachloride is treated with picric acid in benzene solution; it is a brick-red, crystalline substance, and is decomposed by water; on prolonged boiling with benzene, it is decomposed into *picric titanate*, $Ti[O{\cdot}C_6H_2(NO_2)_3]_4$.

Paracresyl titanate, $Ti(O{\cdot}C_7H_7)_4$, is a reddish-brown, crystalline, deliquescent substance; the corresponding *meta*-compound is deliquescent and unstable.

Thymol titanate, $Ti(O{\cdot}C_{10}H_{13})_4$, is a crystalline, very deliquescent substance, readily soluble in most ordinary solvents.

α-Naphthyl titanate, $Ti(O{\cdot}C_{10}H_7)_4$, is a brown, amorphous substance insoluble in neutral liquids; the corresponding *β*-compound was not obtained in a pure condition.

A red, crystalline compound of the composition $TiO_4(C_6H_4{\cdot}CO)_2$ is obtained when salicylic acid is treated with titanium tetrachloride in benzene solution; it is decomposed by water, and combines with ammonia, yielding a yellow substance of the composition

$$TiO_4(C_6H_4{\cdot}CO)_2 + 2NH_3.$$ F. S. K.

Synthesis of a Dihydrocymene. By A. Baeyer (*Ber.*, **26**, 232—234).—The following ethyl dialkylsuccinosuccinates are prepared as formerly described (Abstr., 1892, 1182):—

Ethyl diethylsuccinosuccinate boils at 215° under 15 mm. pressure. The *trans*-compound melts at 65—66°, the *cis*-compound is an oil.

Ethyl dipropylsuccinosuccinate boils at 217—218° under 15 mm. pressure. The *trans*-compound melts at 86—87°; the *cis*-compound is an oil.

Ethyl diisopropylsuccinosuccinate boils at 215—220° under 15 mm. pressure. The *trans*-compound melts at 116—117°; the *cis*-compound is an oil.

From these ethereal salts, the dialkyl diketones are obtained by hydrolysis with dilute sulphuric acid, and by reduction with sodium are converted into the corresponding quinitols. The latter yield dibromides, which, when boiled with quinoline, are converted into dihydro-derivatives of the homologues of benzene. Thus the diethyl compound yields the following:—The *diethyl diketone* in the *trans*-modification melts at 49—50°, in the *cis*-modification at 12°. The *quinitol* is a syrup. The *bromides* are oils. The *dihydrodiethylbenzene* boils at 180—185° (uncorr.), and has a terpene-like odour.

Monalkyl compounds are obtained by heating a mixture of ethyl succinosuccinate and the sodium compound of the same with an alkyl iodide. They are all liquids, dissolve in dilute alkalis without decomposition, and yield diketones, quinitols, and dihydrobenzenes containing one alkyl group. The *methyl* compound boils at 181—182° under 15 mm. pressure; the *propyl* and *isopropyl* compounds boil at about 200°.

Methyl propyl compounds are obtained by heating sodium ethoxide, methyl iodide, and ethyl propylsuccinosuccinate dissolved in benzene for 4—5 hours at 100°.

Ethyl methylpropylsuccinosuccinate is a colourless oil, boils at 195—200° under 15 mm. pressure, and yields a diketone melting at 80°.

Ethyl methylisopropylsuccinosuccinate is a colourless oil, boils at 195—200° under 15 mm. pressure, and yields a diketone, of which the *trans*-modification melts at 64—65°. The quinitol and dibromide are oils. The latter yields

Methylisopropyldihydrobenzene, or *dihydrocymene*, when heated with quinoline. Dihydrocymene boils at 174° (corr.), has a faint odour of turpentine, quickly resinifies on exposure to air, instantaneously decolorises permanganate, and unites with bromine like a terpene. Owing to the small quantity of material, the author was unable to determine if the dihydrocymene is terpinene or an unknown terpene, but it undoubtedly belongs to the class of terpenes, and he considers that the problem of the artificial preparation of a turpentine oil from the simple compounds—acetic acid or acetone or succinic acid—is solved. E. C. R.

Ethers of Homocatechol. By H. Cousin (*Compt. rend.*, **116**, 104—106).—The mono- and di-methyl and mono- and di-ethyl ethers of homocatechol are obtained in the usual way by the action of the

corresponding alkyl iodide on homocatechol in presence of a solution of potassium hydroxide in the corresponding alcohol. The *monomethyl ether* is a colourless liquid, with a strong odour of creosote; it boils at 217—220°, and is insoluble in water, but dissolves in alcohol, ether, and solutions of alkalis; sp. gr. at 0° = 1·1106. The sp. gr. of creosol at 0° is 1·0971, and it boils at 218—219°. The compound solidifies on contact with concentrated alcoholic potash, like the creosol from creosote. The *dimethyl ether* has similar properties, but is insoluble in solutions of alkalis, and boils at 216—217°; sp. gr. at 0° = 1·0668.

The *monethyl ether* boils with partial decomposition at 226—227° under ordinary pressure; sp. gr. at 0° = 1·0928. It is very soluble in water, alcohol, ether, and concentrated solutions of alkalis, but does not solidify in contact with concentrated alcoholic potash. Its aqueous solution gives, with ferric chloride, a green coloration which rapidly changes to brown. The *diethyl ether* is likewise a colourless liquid, with an odour of creosote; it boils at 228°, with partial decomposition; sp. gr. at 0° = 1·0303. It is very soluble in water, and the solution gives no coloration with ferric chloride; it dissolves in alcohol and ether, but is insoluble in solutions of alkalis. The *methyl ethyl ether*, previously described by Hlasiwetz, boils at 223—224°; sp. gr. at 0° = 1·032.

The *diacetyl* derivative, $C_6H_3Me(OAc)_2$ [Me : OAc : OAc = 1 : 3 : 4], is obtained by the action of acetic anhydride on homocatechol. It is a viscous liquid which becomes yellow when exposed to light; it boils at 160—161° under a pressure of 70 mm., and at 263—264° with partial decomposition under ordinary pressure. It is only slightly soluble in water, and the solution gives no coloration with ferric chloride; it dissolves in alcohol and ether, and is decomposed by alkalis, even in dilute solution. Alcoholic potash yields ethyl acetate.

C. H. B.

Action of Chlorine on Phenols. By T. Zincke (*Ber.*, **26**, 311—324).—*The Action of Chlorine on Orcinol.*—The action of chlorine on orcinol is very similar to its action on resorcinol (Abstr., 1891, 689), the first product is a trichlororcinol $C_6MeCl_3(OH)_2$, which, by the further action of chlorine, is converted into pentachlororcinol (1 : 3 : 5-diketomethylpentachlorohexamethylene),

$$CCl_2<\begin{matrix}CO\cdot CCl\\ CO\cdot CCl_2\end{matrix}>CMe,$$

obtained by Stenhouse by the action of hydrochloric acid and potassium chlorate on orcinol. It crystallises in large, transparent prisms, and melts at 120·5°. When boiled with alcohol, it is decomposed, and yields an oily compound. When treated, in a finely-divided state, with water, it is slowly converted into a hydrate, and then into dichloracetyltrichlormethylcrotonic acid, $CHCl_2\cdot CO\cdot CCl{:}CMe\cdot CCl_2\cdot COOH$; the same acid is more easily obtained by employing a solution of sodium acetate and then precipitating with concentrated hydrochloric acid. When the pentachloro-compound is boiled with water, the same acid is obtained, but at once decomposes, and yields a mixture

of ketones. When heated with phosphorus pentachloride at 230°, it yields hexachlorobenzene and heptachlorotoluene (m. p. 119·5°). The latter is identical with the compound prepared by Beilstein and Kuhlberg (*Annalen*, **150**, 306), although they state that it melts at 109°.

Trichlororcinol is very easily obtained by reducing the pentachloro-compound with stannous chloride. It crystallises from water or dilute acetic acid in slender, white needles containing $2\frac{1}{2}$ mols. H_2O, from benzene in transparent cubes containing benzene, and from glacial acetic acid in crystals containing acetic acid. When dry, it melts at 127°, and not at 123°, as stated by Stenhouse. The *acetyl compound* crystallises in white needles, and melts at 130—131°.

Dichloracetyltrichloromethylcrotonic acid, prepared as stated above, crystallises in large, transparent prisms, melts at 115°, and is easily decomposed by the action of bases, and by heating with water. The *methyl* salt crystallises in thick, colourless needles or prisms, and melts at 113°. The *amide*, obtained by treating pentachlororcinol dissolved in benzene with dry ammonia, crystallises in white needles, melts at 175°, has feeble acid properties, and dissolves in sodium carbonate. When the acid is decomposed by water in a distillation flask, the product distils over as an oil which boils at 150—160° under 23 mm. pressure, and is a mixture of the ketones $C_6H_3Cl_3O$ and $C_6H_3Cl_3O_2$. These compounds resemble the crude ketones obtained from pentachlororesorcinol, but could not be characterised, nor do they yield compounds with orthophenylenediamine.

When the acid is decomposed by sodium carbonate, it yields a neutral compound and an acid which, on warming, evolves hydrogen chloride and carbonic anhydride, and is converted into *methyldichloro-metadiketopentene*, $C_5HMeCl_2O_2$. The latter crystallises in white, lustrous leaflets, melts at 80°, and is easily volatile with steam. The neutral compound has the formula $C_6H_3Cl_3O$, crystallises in colourless prisms, melts at 182—183°, and is identical with the compound obtained by Bergmann from the orthodiketochloride $C_6MeCl_3O_2$ (*Inaug. Dissert., Marburg*, 1892).

Trichloracetyltrichloromethylcrotonic acid,

$$CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CCl_2{\cdot}COOH,$$

is obtained by the action of bleaching powder on pentachlororcinol, and also by the action of bleaching powder and acetic or hydrochloric acid on orcinol. Stenhouse erroneously states that when acetic acid is employed, the product is an acid of the composition $C_6H_4Cl_4O_2$ which melts at 130° (*Ber.*, **6**, 575). It crystallises in colourless prisms, melts at 140·5°, and, when strongly heated, decomposes with evolution of carbonic anhydride and hydrogen chloride. When distilled with steam, it yields an oily ketone of the composition C_3Cl_2MeO, which yields chloroform when treated with alkalis. When treated with excess of alkali, it yields chloroform and an acid which has not yet been isolated. When dissolved in sodium acetate and treated with ammonia, it yields a compound of the formula C_5HMeCl_3NO, which crystallises in slender, white needles, melts at 187·5°, is a weak

acid, and yields a sodium salt which crystallises in lustrous leaflets, and is decomposed by water. E. C. R.

Action of Nitrous acid on Isosafrole. By A. Angeli (*Gazzetta*, 22, ii, 445—492; compare this vol., i, 196).—Isosafrole nitrosite dissolves in alcoholic potash with development of heat, and, on pouring the product into water and acidifying, *isonitrosoisosafrole*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}C(NOH){\cdot}COMe,$$

separates; when purified, it forms lustrous, yellow scales, and melts at 98°. On treatment with hydroxylamine hydrochloride, this substance yields a *compound* of the composition $C_{20}H_{17}N_3O_7$, which crystallises in silvery scales melting at 112°; it is soluble in boiling alcohol, benzene, or ethyl acetate, but insoluble in water or light petroleum. The reaction by which it is formed is probably similar to the reaction between hydroxylamine and isonitrosoacetophenone (Scholl, Abstr., 1891, 287) or phenylglyoxal (Müller and v. Pechmann, Abstr., 1890, 51).

Isosafrolenitrolpiperidide, $CH_2{:}O_2{:}C_6H_3{\cdot}C(NOH){\cdot}CHMe{\cdot}C_5NH_{10}$, is prepared by heating the nitrosite with excess of piperidine in alcoholic solution, the liquid is poured into water, and the precipitate crystallised from alcohol; it is thus obtained in white scales melting at 134°. It is soluble in most solvents and acids, has somewhat pronounced basic properties, and gives a *picrate* which crystallises in yellow needles.

Diisonitrosoisosafrole peroxide gives a normal molecular weight by the cryoscopic method in benzene solution. It is very stable towards acids, being precipitated, unaltered, from its sulphuric acid solution by water, and is but little attacked on heating in a sealed tube with hydrochloric acid at 150°; at higher temperatures carbonisation occurs. It is not acted on by acetic anhydride at 210°. Alkaline permanganate oxidises the peroxide with formation of piperonylic acid, and with nitric acid it yields a *nitro*-derivative, $NO_2{\cdot}C_{10}H_7N_2O_4$; this crystallises in yellowish needles melting at 144°, and gives nitropiperonylic acid on oxidation with alkaline permanganate. The peroxide yields a *monobromo*-derivative which forms long, white needles melting at 115°.

On reducing diisonitrosoisosafrole peroxide with zinc dust in acetic acid solution, a *substance*, crystallising in white needles and melting at 210°, is obtained, together with *α-diisonitrosoisosafrole*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}C(NOH){\cdot}CMe{:}NOH;$$

the latter forms lustrous, colourless prisms, and melts at 159°. It is very soluble in alcohol or ethyl acetate, sparingly so in benzene, and is precipitated by carbonic anhydride from its solution in alkalis; it yields a *diacetyl* derivative, $C_{10}H_8N_2O_4Ac_2$, which forms large, white scales melting at 138°, and slowly decomposes in alcoholic solution. α-Diisonitrosoisosafrole is readily oxidised by alkaline ferricyanide solution, yielding the peroxide from which it was obtained.

The facility with which glyoximes yield peroxides on oxidation has been pointed out by Scholl (Abstr., 1891, 315) and others, but the reduction of a peroxide to the corresponding glyoxime described above is the first case of the kind recorded. The author has also succeeded in reducing diphenylglyoxime peroxide to γ-benziledioxime, a reaction which Auwers and V. Meyer failed to effect (Abstr., 1888, 597).

β-Diisonitrosoisosafrole, $CH_2{:}O_2{:}C_6H_3{\cdot}C(NOH){\cdot}CMe{:}NOH$, is obtained by heating α-diisonitrosoisosafrole for an hour at 159°. It forms lustrous, colourless prisms, melts at 209° with decomposition, and is sparingly soluble in alcohol. It yields the same diacetyl derivative as its α-isomeride, and gives the same peroxide on oxidation with ferricyanide. The β-dioxime is also obtained by the action of nitrous acid on the α-compound.

Homoacetopiperone, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}COMe$, is obtained by reducing the peroxide with zinc dust (Abstr., 1892, 1198); it forms almost colourless needles, melts at 38°, and is very soluble in most solvents, but only sparingly so in light petroleum. It yields a *hydrazone*, $C_{16}H_{16}N_2O_2$, which crystallises in yellow needles melting at 97°, and resinifies on exposure to the air. The reduction with zinc dust also yields a *substance* $C_{20}H_{18}N_2O_4$, which forms large, white needles melting at 180°; this gives a normal molecular weight by the cryoscopic method in benzene solution, but its constitution is uncertain. It behaves as a feeble base, and gives a violet colour with concentrated sulphuric acid.

Diisonitrosoisosafrole anhydride, $O<\begin{matrix}N{:}C{\cdot}C_6H_3{:}O_2{:}CH_2\\ |\\ N{:}CMe\end{matrix}$, is obtained on reducing the peroxide with phosphorus sulphide, or tin and hydrochloric acid; it forms highly refractive, lustrous crystals, melts at 86°, and has a normal molecular weight in freezing benzene. It is soluble in benzene, ethyl acetate, or acetone, sparingly so in alcohol, and dissolves without decomposition in concentrated sulphuric acid.

Alcoholic potash converts the peroxide into an *isomeride*, $C_{10}H_8N_2O_4$, which forms microscopic, acicular aggregates melting at 185° with decomposition; it soon turns red in the air, and is soluble in alcohol, acetone, or ethyl acetate, sparingly so in light petroleum. It dissolves readily in alkalis, and separates on acidification; dilute acids convert it into piperonylonitrile, $CH_2{:}O_2{:}C_6H_3{\cdot}CN$. It does not combine with bromine in the cold, and gives a resinous product with phosphorus pentachloride. The *acetyl* derivative, $C_{10}H_7N_2O_4Ac$, which forms almost colourless, lustrous laminæ melting at 129°, is more stable than the parent substance, although it gives the normal molecular weight by the cryoscopic method in acetic acid solution. The *benzoyl* derivative, $C_{10}H_7N_2O_4Bz$, forms small, very hard, lustrous crystals melting at 146° with decomposition. With phenylhydrazine, a *substance*, $C_{22}H_{18}N_4O_2$, is obtained which possibly has the constitution $C_{10}H_7O_2(N_2Ph){\cdot}N_2HPh$; it forms yellow needles melting at about 168°. As the isomeride of the peroxide is readily oxidised by alkaline permanganate with formation of piperonylnitrile, its constitution is probably $CH_2{:}O_2{:}C_6H_3{\cdot}C<\begin{matrix}CO{\cdot}CH_2\\ \|\\ N{-}O\end{matrix}$.

Isosafrole yields a ***nitrosochloride***, $CH_2{:}O_2{:}C_6H_3{\cdot}C_3H_5{:}NOCl$, which is obtained as a white, crystalline powder melting at 132°.

W. J. P.

Action of Nitrous acid on Isoapiole. By A. Angeli and P. Bertolotti (*Gazzetta*, **22**, 493—509).—The action of nitrous acid on isoapiole is, in all respects, analogous to its action on isosafrole (compare preceding abstract).

Diisonitrosoisoapiole peroxide, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}\underset{\underset{NO\cdot ON}{\|}}{C}\!\!-\!\!\!-\underset{\underset{NO\cdot ON}{\|}}{C}Me$, is obtained by dissolving isoapiole in acetic acid and adding potassium nitrite solution; much heat is developed, and the peroxide is deposited. When pure, it forms minute, yellow needles, melting at 169—170°. Like the corresponding isosafrole derivative, it is converted by alcoholic potash into an *isomeride*, probably having the constitution $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}\underset{\underset{N}{\|}}{C}{\cdot}C(NOH){\cdot}\underset{\underset{O}{|}}{C}H_2$, which forms almost colourless needles, melting at 168—170° with decomposition.

Diisonitrosoisoapiole anhydride, $O\!<\!\!\underset{N:CMe}{\overset{N:C\cdot C_6H(OMe)_2{:}O_2{:}CH_2}{|}}$, obtained by reducing the peroxide with tin and hydrochloric acid, crystallises in white needles, and melts at 138°.

On oxidation with alkaline permanganate, the peroxide yields an *acid* which forms lustrous, micaceous scales melting at 61° and containing nitrogen. Its composition could not be determined, owing to the small quantity obtained; a solution of its ammonium salt gives a white precipitate with salts of lead, barium, or calcium. The same acid is formed on oxidising diisonitrosonitroisoapiole.

α-Diisonitrosoisoapiole, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}C(NOH){\cdot}CMe{:}NOH$, prepared by reducing the peroxide with zinc-dust and acetic acid, forms colourless crystals melting at 154°; on oxidation with alkaline ferricyanide solution, it yields the peroxide from which it was derived. The *diacetyl* derivative, $C_{12}H_{12}N_2O_6Ac_2$, forms beautiful, yellow crystals melting at 137—138°. The α-dioxime is converted, by heating at a few degrees above its melting point, into the isomeric ***β-diisonitrosoisoapiole***; this is much less soluble in alcohol than the α-compound, and forms lustrous, colourless crystals melting at 197—198°.

Diisonitrosonitroisoapiole peroxide,

$$CH_2{:}O_2{:}C_6(NO_2)(OMe)_2{\cdot}\underset{\underset{NO\cdot ON}{\|}}{C}\!\!-\!\!\!-\underset{\underset{NO\cdot ON}{\|}}{C}Me,$$

is obtained by the action of nitric acid on the peroxide described above; it forms lustrous, yellow needles melting at 122—123°. The corresponding *bromo*-compound, $C_{12}H_{11}BrN_2O_6$, is prepared by the action of bromine on diisonitrosoisoapiole peroxide; it is obtained in minute, yellow needles melting at 131°. Like the parent peroxide, it is converted by alcoholic potash into an *isomeride*,

$$CH_2{:}O{:}C_6Br(OMe)_2{\cdot}\underset{\underset{N}{\|}}{C}{\cdot}C(NOH){\cdot}\underset{\underset{O}{|}}{C}H_2;$$

this substance forms small, almost colourless crystals, melting at 127—128°. On reduction with zinc-dust and acetic acid, the bromo-derivative of the peroxide yields *diisonitrosobromisoapiole*,

$$C_{12}H_{13}BrN_2O_6,$$

in brilliant crystals, which turn brown at 182° and melt at 220°. An *isomeride* of this substance is obtained on dissolving it in acetic anhydride and precipitating the solution with an alkali; it forms white crystals melting at 94—95°. W. J. P.

Compounds of Malic and Fumaric acids with Aromatic Amines. By E. GIUSTINIANI (*L'Orosi*, 1892, 361—375, and *Gazzetta*, **23**, i, 168—184; compare Abstr., 1892, 820).—Benzylfumarimide crystallises in the anorthic system, $a : b : c = ?$, $\alpha = 85° 54'$, $\beta = 70° 14'$, $\gamma = 80° 44'$, and on reduction with zinc-dust gives a substance of pyrrolic nature. α-Benzylmalimide is obtained in square, monosymmetric laminæ, $a : b : c = 1 : ? : 1{\cdot}23$, $\beta = 69° 17'$, whilst β-benzylmalimide forms orthorhombic prisms, $a : b : c = 0{\cdot}5865 : 1 : 0{\cdot}2253$. The specific rotatory power of both isomerides in aqueous solution varies greatly with the concentration; in a 2·28 per cent. solution, the former gives $[\alpha]_D = -23{\cdot}28°$, whilst a 2·255 per cent. solution of the β-isomeride has $[\alpha]_D = -48{\cdot}56°$. Benzylmalamic acid, obtained from either imide, is slightly lævorotatory.

Aniline hydrogen malate forms small, white crystals melting at about 135°. On heating it at 150—160°, water is evolved, and a substance melting at 190° is obtained, together with malanilide and malanil; at about 200°, the latter loses water, and gives a mixture of fumaric acid and fumaranilide. Malanil is lævorotatory; $[\alpha]_D = -34{\cdot}12°$ in a 0·2244 per cent. aqueous solution.

Paratoluidine hydrogen malate loses water at 150°, giving *paratolylmalimide*, $\begin{matrix}CH(OH)\cdot CO\\ |\\ CH_2\text{——}CO\end{matrix}\!\!>\!N\cdot C_6H_4Me$, and *paratolylmalamide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me.$$

The imide forms minute, yellowish crystals, melts at 184°, and is very soluble in alcohol, ether, or chloroform, less so in water or benzene. On treatment with an alkali, it yields *paratolylmalamic acid*, $C_6H_4Me\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot COOH$, which crystallises in thin, iridescent laminæ. It is soluble in water, alcohol, or ether, and gives very soluble salts. The *silver* salt forms crystalline granules, which are sensitive to light.

Paratolylmalamide is obtained in white needles melting at 195°; it is soluble in alcohol, sparingly so in water or ether, and on treatment with concentrated alkalis yields paratoluidine.

On heating paratoluidine hydrogen malate at above 200°, water and paratoluidine distil, together with *paratolylfumaramide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot CH{:}CH\cdot CO\cdot NH\cdot C_6H_4Me.$$

This substance crystallises in small, yellowish pyramids, melts at 142°, and yields paratoluidine and a fumarate when treated with

alkalis. The *dibromide*, $C_{18}H_{18}N_2O_3Br_2$, forms crystalline granules melting at 168° with decomposition.

Orthotoluidine hydrogen malate is converted into *orthotolylmalamide*, $C_{22}H_{20}N_2O_3$, at 140°; this separates from alcohol in slightly coloured laminæ melting at 179°; it is very soluble in alcohol or ether, sparingly so in water, and yields orthotoluidine with concentrated alkalis. On heating the malate at 200—220°, an oily distillate is obtained, which probably contains *orthotolylfumaramide*. The *dibromide* forms a crystalline powder which blackens at 200°.

W. J. P.

Action of Carbamide on Nitrosamines. By J. Tafel and I. Vogel (*Ber.*, **26**, 335—337).—The regeneration of the original bases from the nitrosamines can usually be brought about by the action of concentrated hydrochloric acid, or by treatment with strong reducing agents, such as tin and hydrochloric acid. In the case of certain tetrahydroquinoline derivatives, the authors find that both these methods cause very great loss of substance, and that a much better yield can be obtained by heating the nitrosamines with carbamide. The reaction corresponds exactly with that of carbamide on nitrous acid, nitrogen and carbonic anhydride being liberated. To carry out the reaction, the nitrosamine is heated with twice the theoretical quantity of carbamide in a distilling flask, the temperature being raised, as the evolution of nitrogen slackens, until it has reached 190—200°; the melt is extracted with warm water, acidified, filtered, and separated from unaltered nitrosamine by extraction with ether or distillation with steam; the residue is then saturated with alkali, and the base isolated in the usual manner.

H. G. C.

Paramidoalkylorthotoluidine. By A. Weinberg (*Ber.*, **26**, 307—308).—An answer to the criticisms of Rosenstiehl (Abstr., 1892, 1319) and Bernthsen (this vol., i, 75) on the author's previous results (Abstr., 1892, 1078).

Metamidophenol and its Derivatives. By M. Ikuta (*Amer. Chem. J.*, **15**, 39—44).—Leonhardt's method of making metamidophenol (D. R. P., 49,060) consists in heating resorcinol with ammonium chloride and aqueous ammonia for 10 hours at 200°. The hydrochloride is thus formed, and after the excess of resorcinol has been removed by treatment with ether, the free base is separated in the usual way and recrystallised from toluene. Metamidophenol crystallises in colourless prisms, melts at 122—123°, and is perfectly stable. In alkaline solution, however, it suffers partial decomposition. The *haloïd salts* and *acid sulphate* are crystalline and stable, subliming with partial decomposition. The *monacetyl derivative* (*metahydroxyacetanilide*) crystallises in colourless needles, and melts at 148—149°. The *diacetyl derivative*, $OAc{\cdot}C_6H_4{\cdot}NHAc$, crystallises in colourless scales, and melts at 101°. The *monobenzoyl derivative* (*metahydroxybenzanilide*) crystallises in colourless, silky needles, and melts at 174°. The *dibenzoyl derivative*, $OBz{\cdot}C_6H_4{\cdot}NHBz$, crys-

tallises in colourless scales, and melts at 153°. The *tribromo-derivative*, $OH{\cdot}C_6HBr_3{\cdot}NH_2$, crystallises in long, bright needles, and melts at 121°. It does not form salts with acids. JN. W.

Oxidation Products of Orthodiamines. By O. FISCHER and O. HEILER (*Ber.*, **26**, 378—386; compare Kehrmann and Messinger, (*J. pr. Chem.*, **46**, 566).—By the oxidation of methylorthophenylenediamine with ferric chloride in alcoholic solution, the hydrochloride of the azonium base is obtained, which has the formula

$$NHMe{\cdot}C_6H_2(NH_2)\begin{matrix}N\\ \diagdown\!\!\diagup\\ NMeCl\end{matrix}C_6H_4$$

[NH : NH_2 : N : N = 5 : 4 : 1 : 2; N : N = 1 : 2]; it crystallises from alcohol, with 2 mols. H_2O, in needles of metallic lustre, has strongly marked basic properties, and gives a red coloration with concentrated sulphuric acid. The *free base*, $C_{26}H_{30}N_6O$, is prepared from the preceding compound by the action of potash, and forms an unstable, red powder.

Anilidobenzeneinduline, $NHPh{\cdot}C_6H_2(NH)\begin{matrix}N\\ \diagdown\!\!\diagup\\ NPh\end{matrix}C_6H_4$, obtained by treating orthamidophenylamine with ferric chloride, crystallises from benzene in brownish-red plates, which remain unmelted below 240°; with concentrated sulphuric acid, a violet-red coloration is obtained, with alcohol, a brown one. The *hydrochloride* is deposited in cantharidine-green plates. The formation of this substance is analogous to that of diamidophenazine from orthophenylenediamine. By the action of dilute sulphuric acid at 150—160° for three hours, it is converted into *anilidobenzeneindone*, $NHPh{\cdot}C_6H_2O\begin{matrix}N\\ \diagdown\!\!\diagup\\ NPh\end{matrix}C_6H_4$ [O = 4]; this crystallises from benzene in brown needles, and gives a green coloration with sulphuric acid, which changes to red on dilution. On heating the induline for six hours with sulphuric acid, *hydroxybenzeneindone*, $HO{\cdot}C_6H_2O\begin{matrix}N\\ \diagdown\!\!\diagup\\ NPh\end{matrix}C_6H_4$, is formed; it is purified by solution in soda, and crystallises from alcohol in slender, lustrous, orange-red needles. Orthamidophenylamine, on distillation with 10 parts of lead oxide, yields phenazine. The amide from paramidodiphenylmetaphenylenediamine may be regarded either as anilidorthoamidophenylamine, $C_6H_3(NHPh)_2{\cdot}NH_2$ [NH : NH : NH_2 = 1 : 3 : 4], or as a paradiamine. On oxidation with lead peroxide, it is converted into an *anilidophenylquinonediimide*, $NH{:}C_6H_3(NPh){\cdot}NHPh$ [NPh=1], which crystallises from light petroleum in orange-red, concentric needles and melts at 98°.

By the action of acids on the diimide in alcoholic solution, or of ferric chloride on the diamine, an induline derivative is obtained, which is deposited from benzene in lustrous, bronze-coloured prisms melting at 235°; the base has well marked tinctorial powers, dissolves in alcohol with a blue colour, and gives a violet-red coloration with concentrated sulphuric acid. This compound is probably represented by one of the following formulæ:—

$NH_2{\cdot}C_6H(NHPh)_2{<}\begin{matrix}-N\\NPh\end{matrix}{>}C_6H_3{\cdot}NPh$ [NH : NH : NH_2 : N : N = 6 : 4 : 3 : 1 : 2; N : N : NPh = 1 : 2 : 4] or [NH : NH : NH_2 : N : N = 5 : 3 : 6 : 1 : 2] and $NH_2{\cdot}C_6H(NPh)(NHPh){<}\begin{matrix}N-\\NPh\end{matrix}{>}C_6H_3{\cdot}NHPh$ [NH : NPh : NH_2 : N : N = 6 : 4 : 3 : 1 : 2; N : N : NH = 1 : 2 : 4].

The *nitrate* and *sulphate* are sparingly soluble.

By the action of nitrous acid on paramidodiphenylmetaphenylenediamine, *anilidoquinonephenylimide*,

$$NPh{:}C_6H_3O{\cdot}NHPh\ [NPh : NH : O = 1 : 3 : 4],$$

is obtained, anilidoquinonephenyldiimide being probably first formed; the phenylenediamine, therefore, reacts as a paradiamine. The compound is deposited from light petroleum in brick-red crystals melting at 125°; with sulphuric acid, a green coloration is obtained, which changes to violet on dilution; with glacial acetic acid, a blue dye is formed. J. B. T.

Products of the Reduction of Orthophenylenediacetonitrile. By C. U. Zanetti (*Gazzetta*, **22**, ii, 510—514).—On reducing a boiling solution of orthophenylenediacetonitrile in absolute alcohol with metallic sodium, two bases are formed which may be separated by taking advantage of the different solubilities of their oxalates in water. The more soluble *oxalate* obtained is probably that of *orthophenylenediethyldiamine*, $C_6H_4(CH_2{\cdot}CH_2{\cdot}NH_2)_2$; the base is an oil, and yields a *picrate* which crystallises in yellow needles melting at 210° with previous decomposition. The *hydrochloride* is deliquescent and very soluble in alcohol.

The second base formed is probably the *imido*-compound, $C_{10}H_{13}N$, corresponding with the above amine; the preparation of such a base is of interest, as it is the type of a new series of closed chain compounds. Its *oxalate* forms small, white needles melting at 216—220° with decomposition, and is sparingly soluble in water. The *benzoyl* derivative separates from boiling alcohol in flat, white needles, and melts at 150—152°.

The author is continuing the investigation. W. J. P.

Compounds of Phenylhydrazine with Metallic Salts. By H. Schjerning (*J. pr. Chem.* [2], **47**, 80—88; see also Abstr., 1892, 1454). —*Zinc phenylhydrazine sulphate*, $Zn(PhN_2H_3)_2SO_4 + H_2O$, crystallises from a hot concentrated mixture of zinc sulphate solution with phenylhydrazine. It is colourless or very pale yellow, but becomes reddish in air by oxidation of the phenylhydrazine. One part of the salt dissolves in 185 parts of water at 19·5°. At 105°, it loses its water of crystallisation; at 170°, it loses phenylhydrazine; above 170°, in a test tube, it explodes slightly. Its reactions are those of both zinc sulphate and phenylhydrazine; a solution of it serves to precipitate certain proteïds

at the ordinary temperature, which are not so precipitated by zinc sulphate solution.

The other salts of this type which the author has prepared are:—*Cadmium phenylhydrazine sulphate*, $5Cd(PhN_2H_3)_2SO_4 + H_2O$; colourless; soluble in 312 parts of water at 17°. The *nickel salt*,

$$Ni(PhN_2H_3)_2SO_4 + H_2O;$$

bright green; soluble in 862 parts of water at 17°. The *cobalt salt*, $Co(PhN_2H_3)_2SO_4 + H_2O$; bright red; soluble in 270 parts of water at 17°. The *manganous salt*, $Mn(PhN_2H_3)_2SO_4 + H_2O$; colourless or pale yellow; very unstable in air; soluble in 55 parts of water at 16°. The *ferrous salt*, $Fe(PhN_2H_3)_2SO_4 + H_2O$; colourless; rapidly oxidises in air; soluble in 240 parts of water at 18°. A. G. B.

Preparation of Methylbenzoïc Anilide. By J. Dupont (*Bull. Soc. Chim.* [3], **7**, 516).—Benzoïc anilide cannot be methylated by Pictet's method (Abstr., 1888, 364). A. R. L.

Orthocyanobenzoïc acid. By S. Hoogewerff and W. A. Van Dorp (*Rec. Trav. Chim.*, **11**, 84—102).—The formation of orthocyanobenzoïc acid from phthalic chloride and ammonia is probably preceded by that of an intermediate compound, $C_6H_4<\begin{matrix}C(NH)\\CO\end{matrix}>O$. The melting point of the acid given by Auger (Abstr., 1888, 953) is too low; the author finds that the acid melts between 180° and 190°, passing, with resolidification, into phthalimide, which then melts at about 230° (compare Allendorf, Abstr., 1891, 1370). The *ammonium* salt forms needles, melts at 160—170° with the evolution of gas, then resolidifies, and again melts at 220—230°; the *methyl* salt crystallises in flat needles, is sparingly soluble in cold water, and melts at 50—51°, whilst the ethyl salt melts at 65—66° (not 70°; see Müller, Abstr., 1886, 803). Phthalamic acid is formed when orthocyanobenzoïc acid is dissolved in concentrated sulphuric acid. The *compound* $S[C(NH)\cdot C_6H_4\cdot COONH_4]_2$ is obtained by treating orthocyanobenzoïc acid with alcoholic ammonium sulphide; it melts at 145°. The formation of the latter compound is analogous to that of thiobenzamide from benzonitrile and ammonium sulphide, and therefore furnishes another argument in favour of the view that the compound obtained from phthalic chloride and ammonia is really orthocyanobenzoïc acid. Phthalic diamide is formed by the action of ammonia on diethyl phthalate. A. R. L.

Acids occurring in Petroleum. By R. Zaloziecki (*Chem. Zeit.*, **16**, 905—907).—The author, having experimented with these compounds, comes to the conclusion that Aschan's theory, which places them amongst the hexahydro-aromatic-carboxylic acids, must not be accepted without further proof. L. de K.

Specific Rotatory Power of the Phenyldibromopropionic acids. By C. Liebermann (*Ber.*, **26**, 245—252).—The author has reexamined the optically active phenyldibromopropionic acids obtained

by Meyer (this vol., i, 93), who gave the specific rotatory power $[\alpha]_D = -13{\cdot}1°$ and $+14°$. By employing only 1 mol. of strychnine to 2 mols. of the acid, and by a systematic fractional precipitation of the two optical antipodes so obtained, he has obtained a more complete separation. The highest specific rotations were $[\alpha]_D = +68{\cdot}3°$ and $[\alpha]_D = -45{\cdot}8°$. The other fractions gave intermediate numbers. According to Van't Hoff's hypothesis, phenyldibromopropionic acid is capable of existing in four optically active modifications and in two modifications of the racemic type. The author is engaged in a further study of these acids.

The author is also engaged in a similar investigation on the dibromo-derivatives of fumaric and maleïc acids. He has prepared many alkaloïd salts of these acids, which will shortly be described, but has not yet succeeded in separating either into its optically active modifications. E. C. R.

Derivatives of the Cresolglycollic acids. By O. Forte (*Gazzetta*, **22**, ii, 525—546).—The author describes a large number of metallic salts of the three cresolglycollic acids. The *ammonium* salts, when heated above 110°, yield the corresponding amides. The *amide* of the ortho-acid, $C_9H_{11}O_2N$, melts at 128°, that of the meta-acid at 111—112°, whilst *paracresolglycollamide* melts at 126—127°. The *anilides* prepared from the ortho-, meta-, and para-acids melt at 110°, 95°, and 109° respectively; the *methyl* salts are colourless liquids of nauseating odours, and boil at 248°, 258°, and 257° respectively. W. J. P.

Dibromogallic acid and its Salts. By A. Biétrix (*Bull. Soc. Chim.* [3], **7**, 411—417).—Dibromogallic acid (m. p. 139°) is conveniently prepared by adding gallic acid to a solution of bromine in chloroform. The *salts* are obtained by mixing solutions of metallic acetates with those of the acid; they are white substances, which are coloured strongly by heating. The *ammonium* salt melts at 175° with decomposition, the *sodium* salt melts at 185° with decomposition, the basic *zinc* salt, $(C_7H_2Br_2O_5)_2Zn_3$, commences to decompose at 110°, and melts at 189°. The basic *lead* salt, $(C_7H_2Br_2O_5)_2Pb_3$, decomposes at 160°, giving off white fumes, and leaving a black residue; and the normal *barium* salt melts between 195° and 200°. The *quinine* salt, $C_{20}H_{24}N_2O_2,C_6Br_2(OH)_3{\cdot}COOH$, is formed as a white precipitate on mixing alcoholic solutions of the acid and of quinine; it is soluble in water, forming a rose-coloured solution, and melts with decomposition at 182—183°. The *strychnine* salt, $C_{21}H_{20}N_2O_2,C_6Br_2(OH)_3{\cdot}COOH$, commences to decompose at 140°, and melts at 190°. A. R. L.

Constitution of the Iodides of Aromatic Sulphonic acids. By R. Otto and J. Tröger (*Ber.*, **26**, 154—155).—When considered in the light of the arguments recently advanced by Selivanoff (this vol., i, 192), the compounds previously described by the authors (Abstr., 1891, 718) as sulphonic iodides would appear to be more correctly denoted "iodyl" derivatives; as a matter of fact, they behave, in most cases, as if they were mixed anhydrides of sulphinic

and hypoiodous acids, the compound $C_6H_5SO_2I$, for example, yielding iodoform, iodophenol, and phenyl bisulphide, on treatment with sodium ethoxide, phenoxide, and mercaptide respectively, as well as the salt of benzenesulphinic acid. F. S. K.

Cryoscopic Studies in the Benzene Series. By J. Haussen (*Bull. Soc. Chim.* [3], **7**, 516—523).—The author finds that certain sulphonic acids of benzene exhibit, in aqueous solutions, molecular depressions far in excess of the constant 19, which holds for the majority of organic substances; the molecular depressions, in fact, approximate to those obtained with the strong monobasic acids. Benzenesulphonic acid gave a mean value of the depression of the freezing point C/P = 0·227, the product of which, by the molecular weight, gives the constant 35·8. Nitrotoluenesulphonic acid

$$[Me : SO_3H : NO_2 = 1 : 2 : 4]$$

gave the constant 35·4, and its sodium salt gave 34·7; whilst nitrosulphobenzoic acid [COOH : SO_3H : NO_2 = 1 : 2 : 4] gave the constant 38·5, its monopotassium salt (modification A) gave 39·9, and modification B gave 41·9.

The *silver* salt of the 1 : 2 : 4-nitrotoluenesulphonic acid crystallises with 1 mol. H_2O, and the *ethyl* salt melts at 68—69°. The *potassium* salt, $COOH{\cdot}C_6H_3(NO_2){\cdot}SO_3K$ (modification A), crystallises in prisms with 1 mol. H_2O. This salt passes into modification B, which crystallises in rhombic tables with 2 mols. H_2O, (1) when it is heated at 280—290° for some hours and then crystallised from water; (2) when, after being dried at 140°, it is heated with phosphoric chloride at 175° for 20 minutes; (3) when it is crystallised in the presence of potassium or ammonium chloride. A. R. L.

Preparation of Pure Ethyl Benzenesulphinate and Ethyl Paratoluenesulphinate. By R. Otto (*Ber.*, **26**, 308—310).—The ethyl benzenesulphinate and paratoluenesulphinate, formerly described by the author and Rössing (Abstr., 1885, 1231), were contaminated with phenylsulphone and tolylsulphone formates. The author has obtained the pure compounds from the product of the action of an alkali salt of the sulphinic acid and ethyl chlorocarbonate as follows:—The ethyl sulphinate is precipitated with water, the mixture rendered faintly alkaline with soda and extracted with petroleum (b. p. 30—40°). The petroleum extract is washed with dilute soda and then with water, and distilled, when the ethyl sulphinate is obtained in a pure condition. The properties of the two compounds have already been described. Ethyl benzenesulphinate has a sp. gr. at 20° = 1·1410; the toluenesulphinate has a sp. gr. = 1·1212. E. C. R.

Behaviour of Indigo when heated with Alkalis. By K. Heumann and C. Bachofen (*Ber.*, **26**, 225—229; compare Abstr., 1891, 456).—The product formed when indigotin is fused with potash does not contain indigo-white, as it yields no precipitate when it is mixed with dilute acid. It was, on the other hand, shown to give the reactions described by Baeyer as typical of indoxyl. This sub-

stance is also formed when indigo is boiled with aqueous potash of sp. gr. 1·45.

Indoxylazobenzenesulphonic acid, a new substance, was obtained as the potassium salt, $C_{14}H_{10}N_3O_4SK$, by adding a solution of the fused mass in dilute sulphuric acid to an aqueous solution of paradiazobenzenesulphonic acid. When dried, it forms green crusts with a metallic lustre; these yield a brownish-red powder, which, when rubbed, acquires a green, metallic lustre. It dyes silk and wool reddish-yellow in feebly acid solution, is decolorised by zinc-dust in alkaline solution, and decomposes suddenly when heated above 230°.

C. F. B.

Derivatives of Diphenyltrichlorethane and their conversion into Stilbene. By K. Elbs (*J. pr. Chem.* [2], **47**, 44—79; compare Abstr., 1889, 713).—Sufficient evidence has now been obtained to enable the author to state generally that compounds of the formula $X_2CH{\cdot}CCl_3$, in which X is the radicle of an aromatic hydrocarbon, a phenol, or a phenetoïl, are converted into compounds of the formula $X{\cdot}CH{:}CH{\cdot}X$, by heating their alcoholic solutions with zinc-dust. In this way, stilbene, paradimethylstilbene (b. p. 304—305°), and metatetramethylstilbene have been obtained (Abstr., 1889, 713).

Diparaxylyldichlorethylene melts at 93°, not 95° (*loc. cit.*); with zinc-dust, it yields paratetramethylstilbene [$Me_2 = 2 : 5$] (m. p. 157°).

Dipseudocumyltrichlorethane, $CCl_3{\cdot}CH(C_6H_2Me_3)_2$, obtained by the action of chloral hydrate on pseudocumene in presence of strong sulphuric acid, crystallises in colourless prisms, melts at 143°, and dissolves sparingly in alcohol, but freely in carbon bisulphide, chloroform, and acetone. Alcoholic potash converts it into *dipseudocumyldichlorethylene*, $CCl_2{:}C(C_6H_2Me_3)_2$, which crystallises in colourless prisms, melts at 118°, and dissolves in alcohol, benzene, carbon bisulphide, and chloroform; the *disulphonic acid*, $CCl_2{:}C(C_6HMe_3{\cdot}SO_3H)_2$, and its *barium* (with 4½ mols. H_2O) and other salts, were prepared; the acid crystallises in white, hygroscopic needles, and is easily oxidised by potassium permanganate to *dipseudocumylketodisulphonic acid*, $CO{:}C(C_6HMe_3{\cdot}SO_3H)_2$, whose *barium* salt was prepared.

Hexamethylstilbene, $C_2H_2(C_6H_2Me_3)_2$ [$Me_3 = 2 : 4 : 5$], obtained by the general method from dipseudocumyltrichlorethane, crystallises in slender, white needles or flat prisms, melts at 161°, and dissolves sparingly in alcohol, but more freely in benzene, carbon bisulphide, and chloroform; it has a violet fluorescence, both in the solid condition and in solution. A *picrate* (crystallising with benzene) was prepared; it melts at 123°. The *bromide*, $C_2H_2Br_2(C_6H_2Me_3)_2$, crystallises in nacreous, colourless laminæ, melts at 238—243° with decomposition, and dissolves sparingly in alcohol, but easily in ether, chloroform, carbon bisulphide, and benzene; during the bromination, *bromo-symmetrical-dipseudocumylethane*, $C_2H_3Br(C_6H_2Me_3)_2$, melting at 177°, and *bromohexamethylstilbene bromide*, $C_6H_2Me_3{\cdot}CHBr{\cdot}CHBr{\cdot}C_6HMe_3Br$, melting about 240°, were also obtained. During the reduction of dipseudocumyltrichlorethane, a small quantity of *asymmetrical dipseudocumylethane* (m. p. 117—120°) is formed.

α-Dinaphthostilbene, $C_2H_2(C_{10}H_7)_2$, is prepared by the reduction of α-dinaphthyltrichlorethane (for the preparation of which a new method is detailed; compare Grabowski, Abstr., 1878, 508); it is separated from the asymmetrical α-dinaphthylethane which accompanies it by crystallisation from glacial acetic acid, in which it is less soluble, and purified by conversion into the *picrate*, $C_2H_2(C_{10}H_7)_2 + 3C_6H_3N_3O_7$, which melts at 210°. α-Dinaphthostilbene crystallises in yellowish, silky laminæ, melts at 161°, and dissolves sparingly in alcohol, more freely in ether and glacial acetic acid, and easily in chloroform, carbon bisulphide, and benzene; its solutions fluoresce violet; oxidation converts it into 1-naphthoic acid. The *bromide* crystallises in colourless needles and laminæ, melts at 211°, and dissolves best in benzene.

Asymmetrical α-dinaphthylethane crystallises in colourless laminæ, melts at 136°, and is more soluble than dinaphthostilbene; its solutions fluoresce violet. It yields no picrate. *Dibromodinaphthylethane* melts at 215° and is sparingly soluble.

Concerning paradihydroxystilbene and the nitrohydroxydiphenyltrichlorethanes, see Abstr., 1889, 997.

β-Dinaphthyloxidetrichlorethane, $CCl_3{\cdot}CH{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}O$, is the product of the condensation of chloral hydrate and β-naphthol by sulphuric acid; it crystallises in large, colourless, strongly-refractive prisms, melts, with decomposition, at 241°, and dissolves best in boiling chloroform and xylene. Reduction converts it into ethylidene-β-dinaphthylene oxide (m. p. 273°; Abstr., 1887, 271). *α-Dinaphthyloxidetrichlorethane*, from α-naphthol and chloral hydrate, crystallises in prisms and melts at 238—239° with decomposition; it is being investigated.

Dianisyltrichlorethane [$CH{\cdot}CCl_3 : OMe = 1 : 4$], the product of the condensation of chloral hydrate and anisoïl, crystallises in prisms, melts at 92°, and is freely soluble. By reduction, it yields diparamethoxystilbene, which fluoresces violet (compare Kopp, Abstr., 1892, 718).

α-Diethoxynaphthyltrichlorethane, $CCl_3{\cdot}CH(C_{10}H_6{\cdot}OEt)_2$, from chloral hydrate and 1-naphthyl ethyl ether, generally separates from its solutions as a crystalline powder; it melts at 198—200°, and dissolves best in xylene and benzene; it does not fluoresce.

α-Diethoxydinaphthostilbene, $C_2H_2(C_{10}H_6{\cdot}OEt)_2$, obtained by reducing the last compound, exists in two modifications; the stable form crystallises in sulphur-yellow tables, the unstable form in colourless needles; both fluoresce blue when solid and in solution. The unstable form is obtained by recrystallising the stable form from boiling glacial acetic acid or alcohol; it gradually changes into the stable form at 100°, and rapidly at 160—170°. The stable modification melts at 185—186°, and boils at a higher temperature undecomposed; it dissolves best in boiling xylene and benzene. The *picrate* (2 mols. picric acid) melts at 236—238°. The *bromide* has not been purified.

β-Diethoxydinaphthyltrichlorethane, from 2-naphthyl ethyl ether and chloral hydrate, is a crystalline powder; it melts with decomposition at 206°, dissolves best in boiling xylene and benzene; by reduction,

it yields a substance which melts at 186°, but has not been satisfactorily identified as β-diethoxydinaphthostilbene.

The paper concludes with a table, showing the solubility of the above compounds in alcohol. A. G. B.

Condensation Products of Amidophenols. By E. HAEGLE (*Ber.*, **26**, 394).—Benzylideneparamidophenol melts at 183°, hydroxybenzylideneorthoamidophenol at 185°, and cinnamylideneparamidophenol at 203°, instead of at 163°, 175°, and 223° respectively, as previously stated (compare Abstr., 1892, 1451). J. B. T.

Solubility of Triphenylmethane in Benzene. By C. E. LINEBARGER (*Amer. Chem. J.*, **15**, 45—49).—The solubility of triphenylmethane in benzene is shown in the following table.

Temperature.	Parts $CHPh_3$ per 100 parts C_6H_6.	Temperature.	Parts $CHPh_3$ per 100 parts C_6H_6.
3·9°	3·90	37·5°	10·48
4·0	4·06	42·0	19·61
12·5	5·18	44·6	22·64
13·0	5·51	50·1	30·64
16·1	6·83	55·5	40·51
19·4	7·24	71·0	140·0
23·1	8·95	76·2	319·67

Changes of curvature occur at 3·9°, 27·5°, 76·2°, and 94·3°. At 3·9°, there exist together benzene (solid), a molecular compound of triphenylmethane and benzene, $CHPh_3,C_6H_6$ (solid), a solution of triphenylmethane in benzene, (liquid), and a mixture of the vapour of triphenylmethane and benzene (gas). At 37·5°, the benzene is no longer solid, and the molecular compound has begun to decompose, so that triphenylmethane (solid) is present. The molecular compound melts at 76·2° in a closed tube. The melting point of triphenylmethane is 94·3°. JN. W.

Phenolphthaleïn. By P. FRIEDLÄNDER (*Ber.*, **26**, 172—179).—The constitutional formula ascribed by Baeyer to phenolphthaleïn, namely, $CO<^{C_6H_4}_{O}>C(C_6H_4\cdot OH)_2$, explains all the reactions in a satisfactory manner, but it is difficult to understand how the salts of such a colourless substance should be colouring matters if they are formed by the simple substitution of a metal for the hydrogen of one of the hydroxyl groups; the author has, therefore, endeavoured to ascertain whether, in the formation of the salts, an intramolecular change takes place with formation of a quinone derivative having the constitution $O:C_6H_4:C(C_6H_4\cdot ONa)\cdot C_6H_4\cdot COONa$, which would correspond with the quinone formulæ proposed by Nietzki for rosaniline and rosolic acid. To test the truth of the supposition, an alkaline solution of phenolphthaleïn was treated with hydroxylamine, with the result that an oxime of the sodium salt,

$$OH\cdot N:C_6H_4:C(C_6H_4\cdot OH)\cdot C_6H_4\cdot COONa,$$

was readily obtained on adding acetic acid. The oxime separates as a bright yellow, crystalline precipitate, which is purified by washing with water and alcohol. It is scarcely soluble in the common solvents and melts at 212° with decomposition. It is dissolved by alkalis with the formation of two series of salts, and yields a *hydrochloride*, and a crystalline *acetyl* derivative insoluble in alkali. When hydrolysed with dilute sulphuric acid, it is converted into amidophenol and *parahydroxyorthobenzoylbenzoic acid*, $HO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot COOH$, which crystallises in white plates, and melts with decomposition at 210°, the former being probably obtained by an intramolecular change from the phenylhydroxylamine which should be the first product of the hydrolysis. Fusion with alkali gives similar results, the benzoylbenzoic acid being further resolved into benzoic and parahydroxybenzoic acids. H. G. C.

Trihydroxyaurin from Catechol. By N. Caro (*Ber.*, **26**, 254—255; see also Abstr., 1892, 855 and 1469).—*Methylenedicatechol*, $CH_2[C_6H_3(OH)_2]_2$, is obtained by boiling a solution of catechol, formaldehyde, and a few drops of hydrochloric or sulphuric acid for some time. It crystallises in needles, melts at 220° with decomposition, and is easily soluble in alkalis.

Trihydroxyaurin, $O<\begin{matrix}C_6H_3\cdot OH\\ |\\ C[C_6H_3(OH)_2]_2\end{matrix}$, cannot be obtained pure by the condensation of methylenedicatechol with catechol. It is obtained by Nencki and Schmidt's method for the preparation of aurines (*J. pr. Chem.* [2], **23**, 547). It crystallises in leaflets, dissolves in alcohol with a beautiful red coloration, and yields dyes with mordants. E. C. R.

Anisolines, a New Class of Colouring Matters, and their Constitution. By P. Monnet (*Bull. Soc. Chim.* [3], **7**, 523—527).—As is known, rhodamines are obtained by the interaction of dialkylmetamidophenols and phthalic anhydride; the *anisolines* are formed by heating the potassium derivatives of the rhodamines with alkyl chlorides. The simplest anisoline, $\begin{matrix}CO\cdot O\\ |\\ C_6H_4\end{matrix}>C[C_6H_3(OEt)\cdot NEt_2]_2$, derived from diethylmetamidophenol, is obtained by dissolving the corresponding rhodamine hydrochloride in boiling water, and pouring the solution into one of potassium hydroxide. The potassium salt which separates is dried at 100°, and heated in a sealed tube with ethyl chloride and alcohol at 120° for four hours. The melt is poured into water, and the solution heated to expel the alcohol; an excess of hydrochloric acid is now added, and the *hydrochloride* finally precipitated with sodium chloride; it is a green powder with metallic lustre. In preparing benzylated anisolines, the mixtures must be heated to 140°; they readily yield sulphonic acids.

The anisolines colour unmordanted fibres (especially cotton) a magnificent reddish-violet of great fastness. A. R. L.

Substitution Products of the Naphthyl Ethers. By J. Sachs (*Ber.*, **26**, 252—254).—*Dichloro-β-dinaphthyl oxide*, $C_{20}H_{12}Cl_2O$, is

prepared by the action of phosphorus pentachloride on β-dinaphthyl oxide. It crystallises in beautiful, colourless prisms, and melts at 128°.

Dibromo-β-dinaphthyl oxide is obtained by adding bromine to a solution of the β-dinaphthyl oxide in carbon bisulphide. It crystallises with 3 mols. of benzene in stout, transparent prisms which melt at 89°. When freed from benzene by heating at 80°, it melts at 132°.

Dinitro-β-dinaphthyl oxide is obtained by adding nitric acid to a solution of the oxide in acetic acid. It crystallises in indistinct, yellow needles, and melts at 145°.

Hexanitro-β-dinaphthyl oxide is obtained by adding the oxide to well cooled fuming nitric acid. It forms yellow crystals, and decomposes at 270° without melting.

Dibromodinitro-β-dinaphthyl oxide, obtained by brominating the dinitro-compound, crystallises in indistinct, yellow prisms, and melts at 87°.

Dichlorodinitro-β-dinaphthyl oxide is an orange-yellow, crystalline compound, and melts at 76°.

Dibromo-α-dinaphthyl oxide separates in beautiful colourless crystals which do not contain benzene, and melts at 158°. E. C. R.

Compounds of Phthalic acid with Phenols. By R. Meyer (*Ber.*, **26**, 204—210; compare Abstr., 1891, 1029, and especially 1485, of which paper the present one is but an amplification).—The product of the action of β-naphthol on phthalic chloride is not, as hitherto supposed, β-naphthofluoran,

$$CO<\begin{matrix}C_6H_4\\-O-\end{matrix}>C<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O,$$

but consists mainly of β-naphthyl phthalate, $C_6H_4(COOC_{10}H_7)_2$ or $CO<\begin{matrix}C_6H_4\\-O-\end{matrix}>C(OC_{10}H_7)_2$, mixed with a small quantity of the fluoran. The phthalate was identified by hydrolysing it by treatment with potash, when it yielded phthalic acid and β-naphthol. β-Naphthofluoran forms colourless needles, and melts at 293°; its solution in sulphuric acid exhibits a reddish-yellow fluorescence. It may also be prepared, although only in small quantity, by heating phthalic anhydride with β-naphthol for some time at 220°. α-Naphthofluoran has already been obtained by Grabowski (*Ber.*, **4**, 661); the author confirms his results. With pseudocumenol, $C_6H_2Me_3{\cdot}OH$ [$Me_3 : OH = 1 : 2 : 4 : 5$], melting at 67°, phthalic chloride yields the corresponding phthalate, in brilliant needles melting at 118—119°; no fluoran is formed. Paracresol also yields the phthalate in brilliant, colourless prisms melting at 83—84°; a trace of a fluoran was possibly formed, but only a very feeble fluorescence was exhibited on dissolving the crude product of the reaction in sulphuric acid. C. F. B.

Benzeneazonaphthalene and Tolueneazonaphthalene. By R. Nietzki and R. Zehnter (*Ber.*, **26**, 143—145).—*Benzene-α-azo-*

naphthalene, $C_{16}H_{13}N_2$, prepared by diazotising benzene-α-azonaphthylamine and decomposing the product with boiling alcohol, crystallises in dark red plates, melts at 63·5°, and dissolves in concentrated sulphuric acid with a reddish-violet coloration. The corresponding *hydrazo*-compound, $NHPh{\cdot}NH{\cdot}C_{10}H_7$, prepared by reducing the azo-derivative with alcoholic ammonium sulphide, crystallises in yellowish plates, melts at 125°, and oxidises very readily on exposure to the air; its *diacetyl* derivative melts at 264°.

Diamidophenylnaphthalene is formed when benzenehydrazonaphthalene is treated with mineral acids: it crystallises in greyish plates, and melts at 64°. The *hydrochloride*, $C_{16}H_{14}N_2,2HCl$, is a colourless, crystalline compound; the *sulphate* is sparingly soluble in water. The *diacetyl* derivative, $C_{20}H_{18}N_2O_2$, crystallises in needles, and melts at 285°. The *tetrazo*-derivative combines readily with naphthionic, salicylic, and naphtholsulphonic acids yielding azo-dyes, which can be fixed on unmordanted cotton, but which are of little value as dyes compared with the corresponding derivatives of benzidine and tolidine.

Orthotoluene-α-azonaphthalene, $C_{17}H_{14}N_2$, obtained from orthotoluene-α-azonaphthylamine, crystallises in small, red plates, and melts at 52°; the corresponding *hydrazo*-compound, $C_{17}H_{16}N_2$, melts at 107°, and forms a *diacetyl* derivative melting at 252°.

Diamidotolylnaphthalene, prepared by treating the hydrazo-compound with mineral acids, melts at 76°, forms a sparingly soluble *sulphate*, and a *hydrochloride* of the composition $C_{17}H_{16}N_2,2HCl$; its *diacetyl* derivative, $C_{21}H_{20}N_2O_2$, melts at 261° with decomposition. The *tetrazo*-derivative yields azo-dyes, which are similar to those obtained from diamidophenylnaphthalene. F. S. K.

Sulphonic Derivatives of Naphthalene. By R. Otto, A. Rössing, and J. Tröger (*J. pr. Chem.* [2], **47**, 94—104).—The first part of this paper consists of a review of our knowledge of 1- and 2-naphthalenesulphinic acids and their reactions (compare this Journal, 1877, i, 315; *Zeits. Chem.*, 1869, 710; Abstr., 1892, 623).

α-Naphthylmethylsulphone forms rhombic crystals, of which full measurements are here given; it melts at 102—103°. β-Naphthylmethylsulphone melts at 142—143°, not 139—140° (Abstr., 1892, 623).

α-Naphthylethylsulphone, from sodium α-naphthylsulphinate and ethyl iodide, crystallises in small needles, melts at 88—89°, and dissolves easily in alcohol, glacial acetic acid, and benzene, but not in water. *β-Naphthylethylsulphone*, from sodium β-naphthylsulphinate and ethyl bromide, forms ill-defined crystals, melts at 43—45°, and dissolves in ether, alcohol, and benzene, but not in water.

A. G. B.

Constitution of Camphor, Oil of Turpentine, and of their Principal Derivatives. By L. Bouveault (*Bull. Soc. Chim.* [3], **7**, 527—538).—A polemical paper. The various constitutional formulæ which have been assigned to the members of the terpene series are discussed, and the author's line of argument finally leads him to the adoption of the formulæ proposed by Wallach. A. R. L.

Novel Transformation of Camphor into Camphoric Acid. By A. Angeli (*Ber.*, **26**, 58—50).—Nitrosocamphor,

$$C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}NOH\end{matrix},$$

is readily converted into the imide of camphoric acid (Winzer, Abstr., 1890, 1152) when it is heated on the water-bath for five minutes with concentrated sulphuric acid (10 parts). Seeing, therefore, that the carboxyl groups in camphoric acid originate from the group $-CO\cdot CH_2-$ in camphor, the author is of opinion that the relation of camphor to camphoric acid is a simple one, involving no intramolecular changes. A. R. L.

Conversion of Nitrosocamphor into Camphoric Imide. Camphordioximes. By O. Manasse (*Ber.*, **26**, 241—245).—The author confirms Angeli's results (preceding abstract). Nitrosocamphor is converted into camphoric imide by treating it with concentrated sulphuric acid; by heating it at 100° in a solution of acetic acid and acetic anhydride saturated with hydrogen chloride, or by warming it with concentrated hydrochloric acid. By the last method only a small yield is obtained, as the greater part is converted into camphoramic acid, $COOH\cdot C_8H_{14}\cdot CO\cdot NH_2$.

Camphordioximes, $C_8H_{14}(C{:}NOH)_2$.—The author has obtained three isomeric dioximes. The α- and β-dioximes are obtained by the action of hydroxylamine acetate on nitrosocamphor; the γ-dioxime is obtained by the action of free hydroxylamine. The α- and β-dioximes are separated by shaking the mixture with cold alcohol, which only dissolves the α-dioxime. The α-dioxime melts at 181—182° with decomposition; the β-dioxime at 220—221° with decomposition. The γ-dioxime crystallises in white leaflets, melts at 131—132° without decomposition, and when further heated is converted into the α-dioxime.

The α- and β-dioximes, when heated for six hours with concentrated sulphuric acid at 65°, are unaltered, whereas the γ-dioxime under the same conditions is converted into the α-dioxime. E. C. R.

Terpenes and their Derivatives. By J. W. Brühl and R. Braunschweig (*Ber.*, **26**, 284—292; see also Abstr., 1892, 1100; Trans., 1892, 1089).—Camphoric acid may be distilled unchanged in a rapid stream of carbonic anhydride or other indifferent gas. The best method of preparing camphoric anhydride is to heat camphoric acid in a slow stream of carbonic anhydride until water ceases to pass over, and then to distil the anhydride in a rapid stream of the gas.

Orthoalkyl hydrogen camphorates are very easily obtained by heating camphoric anhydride with an alcohol, or the sodium derivative of an alcohol.

Orthomethyl and orthoethyl hydrogen camphorates are obtained by heating camphoric anhydride with methyl or ethyl alcohol in a closed vessel at 160° for 12 hours. Orthomethyl and orthoethyl sodium camphorates are obtained by distilling a mixture of camphoric anhydride, methyl or ethyl alcohol, and sodium.

Orthomethyl hydrogen camphorate crystallises from water in crystals which have already been described. It has now been obtained from light petroleum in two other forms, which are hemihedral, and belong to the rhombic system,

$$a : b : c = 0{\cdot}7855 : 1 : 0{\cdot}4949.$$

The one form is prismatic, of rhombic habit; the other tabular, of hexagonal habit.

Allomethyl hydrogen camphorate crystallises from light petroleum in beautiful prismatic crystals belonging to the rhombic system, $a : b : c = 0{\cdot}7815 : 1 : 0{\cdot}7609$.

The ethereal salts of camphoric acid, with the exception of the orthoethyl salt, distil unchanged under diminished pressure, and the following constants were determined.

The orthomethyl salt boils at 198·5° under 15 mm., and melts after distillation at 77°. The allomethyl salt boils at 193° under 15 mm., and melts at 86°. The orthoethyl salt boils at 204° under 14 mm. pressure, with partial decomposition. The alloethyl salt boils at 196·5° under 13 mm., and melts at 57°.

The author points out that the above synthesis of the ortho-ethereal salts from camphoric anhydride is a weighty argument in favour of the view that camphoric acid is a dicarboxylic acid.

Ethyl hydrogen camphorate, when warmed with phenylhydrazine, yields two isomeric compounds of the formula $C_{17}H_{22}N_2O_2$, which may be separated by fractional crystallisation from light petroleum. The one compound crystallises in nodules, and melts at 137°; the other in slender needles, and melts at 126—127°. E. C. R.

Action of Phenylhydrazine on Cantharidin. By L. Spiegel (*Ber.*, **26**, 140—143; compare Abstr., 1892, 999; and this vol., i, 40). —When cantharidinphenylhydrazone is treated with bromine in boiling glacial acetic acid solution, it is converted into a compound of the composition $C_{16}H_{18}N_2Br_2O_3$, which crystallises in slender, colourless needles, and melts at 245° (corr.); under the same conditions, the hydrate of the hydrazone yields not only the dibromo-derivative melting at 245°, but also a substance which crystallises from alcohol in yellowish prisms, melts at 194° (corr.), and is probably a *diacetyl* derivative of the composition $C_{16}H_{16}N_2Br_2O_4Ac_2$.

A bright yellow substance, which seems to be a mixture of the nitro-, $C_{16}H_{17}N_2O_3{\cdot}NO_2$, and dinitro-, $C_{16}H_{16}N_2O_3(NO_2)_2$, derivatives, is formed when cantharidinphenylhydrazone is treated with ice-cold nitric acid; it crystallises in slender, canary-yellow needles, does not melt at 320—330°, and gives an intense red coloration with alkalis; on reduction with stannous chloride and hydrochloric acid, it yields cantharidinimide.

When cantharidinphenylhydrazone is reduced with sodium amalgam and acetic acid in alcoholic solution, it gives cantharidin; the constitution of the latter is possibly represented by the formula

$$\begin{matrix} CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO \\ | \qquad\qquad\quad | \\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CO \end{matrix} > O.$$

F. S. K.

Action of Alkalis on the Alkyl Iodides of Pyridine and similar Bases. By H. DECKER (*J. pr. Chem.* [2], **47**, 28—44; compare Abstr., 1892, 729, 879).—1-Methyl-2-pyridonè (Abstr., 1892, 729) boils at 250°, not 240° (Pechmann and Baltzer, Abstr., 1892, 209). 1-Ethyl-2-pyridone boils at 249—250°, not 246—248° (*loc. cit.*). 1'-Methyl-2'-quinolone boils at 324° (728 mm.); this compound has been described by Friedländer and Müller as methylpseudocarbostyril (Abstr., 1887, 977), and is probably also identical with a compound (m. p. 73°) obtained by Bernthsen and Hess (Abstr., 1885, 558) and with one (m. p. 72—75°) obtained by Ostermayer (Abstr., 1885, 813). 1'-Ethyl-2'quinolone (Friedländer and Müller's ethylpseudocarbostyril; Abstr., 1885, 988) boils at 316—318°, and remains superfused for a long time. 1'-Methylisoquinolone melts at 38—40°; its *platinochloride* (with 2 mols. H_2O) is described.

1'-*Methylnitroisoquinolone* is obtained by oxidising nitrosoquinoline methiodide in alkaline solution, best by potassium ferricyanide; it crystallises in yellow needles, melts, but not sharply, at 120°, and dissolves easily in benzene, ether, and alcohol; its *platinochloride* melts with decomposition between 165° and 170°.

The preparation of the compounds mentioned in this abstract can be quantitatively effected by titrating an alkaline solution of potassium ferricyanide with a solution of the quinoline alkyl iodide until the yellow colour of the ferricyanide disappears. A. G. B.

Combination of Quinoline with Silver Haloïds. By R. VARET (*Compt. rend.*, **116**, 60—62; compare Abstr., 1891, 732 and 838, and 1892, 1483).—When quinoline is heated at 60°, it dissolves considerable quantities of silver cyanide without appreciable reduction, and when the solution cools it deposits large, transparent crystals of quinoline argentocyanide, $AgCN,2C_9H_7N$. This compound is decomposed by water and by heat; it dissolves readily in warm quinoline, but if the temperature is raised much above 60° the silver cyanide separates as a flocculent precipitate.

Silver bromide, chloride, and iodide are almost insoluble in quinoline, but if triturated with the latter and allowed to remain in contact with it for some time in the dark and out of contact with air, compounds of the general composition AgX,C_9H_7N are formed. Quinoline argentobromide and quinoline argentochloride crystallise in slender needles; the argentoiodide forms a white, amorphous compound. They are all decomposed by water and by heat, and alter when exposed to air and light. C. H. B.

Synthesis of Ring Compounds from Benzene Derivatives with Open Side-chains. By P. SCHAD (*Ber.*, **26**, 216—224).—The following new synthesis of indazole is probably more convenient than those previously described. A solution of isatin and sodium nitrite in dilute aqueous soda is poured into cooled dilute sulphuric acid, the liquid is saturated with sulphurous anhydride, and excess of stannous chloride is finally added; indazolecarboxylic acid then separates, orthodiazo- and orthohydrazine-phenylglyxoylic acids having been doubtless formed as intermediate product. The acid,

when heated above its melting point, loses carbonic anhydride, and forms indazole. *Indazolecarboxylic acid*, $C_6H_4<\begin{matrix}C(COOH)\\ |\\ N\end{matrix}\!\!>N$, forms transparent, rhombic plates, melts with decomposition at 258—259°, yields an *ammonium salt*, $C_7H_5N_2\cdot COONH_4 + \frac{1}{2}H_2O$, as sparingly soluble, colourless needles, and insoluble salts with solutions of salts of the heavy metals; with acetic anhydride, it yields an acetyl derivative, but it does not form a nitroso-derivative. n-*Methylindazole*, $C_6H_4<\begin{matrix}CH\\ |\\ N\end{matrix}\!\!>NMe$, is obtained by heating indazole with methyl iodide at 100° in a tube; it forms lustrous plates melting at 35°. The *nitrosamine* of *orthomethylamidophenylglyoxylic acid*, $C_9H_8N_2O_4$, was obtained by treating methylpseudoisatin with nitrous acid in the cold; it crystallises in groups of yellowish-white needles, melts with decomposition at 107°, gives Liebermann's reaction, and is very unstable, the nitroso-group being readily eliminated under the influence of reducing agents, with re-formation of the original acid. *Paramethylindazole*, $C_6H_3Me<\begin{matrix}CH\\ |\\ N\end{matrix}\!\!>NH$, and its *carboxylic acid* may be obtained from paramethylisatin in the same way as the above-mentioned compounds from isatin itself. The acid forms colourless needles, melting with decomposition at 285—286°; the indazole colourless needles melting at 115°.

β-Diamidodiphenic acid, $C_{14}H_{12}N_2O_4$, obtained by reducing β-dinitrodiphenic acid (from phenanthraquinone and nitric acid), is a very insoluble substance, and chemically very inert; by acidifying a hot solution of its ammonium salt with acetic acid, it is obtained in small, colourless needles which char above 300°. It is probably the *ortho*-diamido-compound, for when heated with lime it yields ammonia; now orthodiamidodiphenyl is known to be converted into carbazole by the action of heat, and carbazole yields ammonia when heated with lime.

The *phenylhydrazone* of *hydroxyphenylglyoxylic acid*,

$$HO\cdot C_6H_4\cdot C(N_2HPh)\cdot COOH,$$

was prepared. The action of sodium phenolate on ethyl chloroxalate results in the formation of diphenyl oxalate.

Calcium phenylenediacetate, when distilled, chars, but decomposes to some extent into calcium carbonate and *β-ketohydrindene*,

$$C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>CO.$$

This crystallises in colourless needles, and melts at 58°; its *phenylhydrazone* forms yellowish tables melting at 120°, and its *oxime*, C_9H_9NO, colourless needles, melting at 152°. When phenylenediacetic acid is mixed with red phosphorus, the mixture treated with bromine, and the bromo-acid thus formed is decomposed with water, it yields the *lactonic acid* of *phenylacetoglycollic acid*,

$$C_6H_4<\begin{matrix}CH(COOH)\\ CH_2\text{——}CO\end{matrix}\!\!>O.$$

This melts at 140°, and crystallises from water with $1\frac{1}{2}H_2O$ in groups of needles which melt at 85°. By digesting its aqueous solution with barium carbonate, the *barium salt*, $(C_{10}H_7O_4)_2Ba + 4H_2O$, may be obtained in colourless plates. When boiled with an alkali, the lactone ring is broken, but, on neutralising the solution, a salt of phenylacetoglyoxylic acid is at once re-formed. C. F. B.

Glyoxalinedicarboxylic acids. By MAQUENNE (*Ann. Chim. Phys.* [6], **24**, 522—548; compare Abstr., 1890, 1439; 1891, 330).—*2-Ethyl-β-pyrazole-4 : 5-dicarboxylic acid* (*ethylglyoxalinedicarboxylic acid*), $C_7H_8N_2O_4 + H_2O$, is obtained when dinitrotartaric acid is treated with propaldehyde in presence of ammonia; it crystallises in colourless needles, loses its water at 2°, and decomposes into carbonic anhydride and 2-ethyl-β-pyrazole when heated more strongly.

2-Isopropyl-β-pyrazoledicarboxylic acid, $C_8H_{10}N_2O_4 + H_2O$, prepared from isobutaldehyde in like manner, crystallises in prismatic needles, loses its water at 182°, and yields 2-isopropyl-β-pyrazole on distillation.

2-Isobutyl-β-pyrazoledicarboxylic acid, $C_9H_{12}N_2O_4$, prepared from isovaleraldehyde, is a crystalline, sparingly soluble powder, and gives 2-isobutyl-β-pyrazole on distillation; the *ammonium* salt,

$$C_9H_{11}N_2O_4{\cdot}NH_4,$$

crystallises in slender needles.

2-Hexyl-β-pyrazoledicarboxylic acid, $C_{11}H_{16}N_2O_4$, is formed from œnanthaldehyde under the conditions already stated; it crystallises in small, yellow plates, and yields 2-hexyl-β-pyrazole melting at 45—46° on distillation.

2-Phenyl-β-pyrazoledicarboxylic acid, $C_{11}H_8N_2O_4$, prepared from benzaldehyde, crystallises in lustrous plates, and is almost insoluble in water; the phenyl-β-pyrazole obtained from it has been described (*loc. cit.*). F. S. K.

4-Phenylpyrazole. By E. BUCHNER and M. FRITSCH (*Ber.*, **26**, 256—258; compare next abstract).—*4-Phenylpyrazole-3 : 5-dicarboxylic acid*, $C_3N_2HPh(COOH)_2$, is prepared by heating methyl diazoacetate with methyl phenylpropiolate or with methyl α-bromocinnamate at 80—90° and hydrolysing the product; it crystallises from water in colourless needles, melts at 243° with decomposition, and is not affected by potassium permanganate in alkaline solution. Its constitution is shown by its failure to form a fluorescein derivative. The *calcium salt* crystallises with $4H_2O$. *4-Phenylpyrazole*, $C_3N_2H_3Ph$, is obtained by heating the carboxylic acid at 250—270°; it crystallises in needles, melts at 78°, boils at 280—290°, and reduces ammoniacal silver solution. The *hydrochloride* melts at 144—145°; the *platinochloride* crystallises with $2H_2O$; it softens at 193° with slight decomposition, solidifies on further heating, and melts at about 218°. The *benzoyl* derivative crystallises in needles melting at 59°.

J. B. T.

5-Phenylpyrazole. By E. BUCHNER and H. DESSAUER (*Ber.*, **26**, 258—261; compare preceding abstract).—By the action of ethyl cinnamate on ethyl diazoacetate at 100°, *diethyl 5-phenylpyrazoline-3 : 4-dicarboxylate* is formed, and has been previously described as "ethyl cinnamodiazoacetate"; it melts at 79°, and yields ethyl phenylpyrazoledicarboxylate on treatment with bromine. The *silver salt* forms a lemon-coloured, flocculent precipitate. *Dimethyl phenylpyrazolinedicarboxylate* melts at 105°. The *3-ethyl-4-methyl salt*, prepared from methyl cinnamate and ethyl diazoacetate, melts at 76°. The *3-methyl-4-ethyl salt* from ethyl cinnamate and methyl diazoacetate, melts at 107°. The *amide*, $C_9H_8N_2(CONH_2)_2$, melts at 228° with decomposition. The *acid*, $\begin{matrix}CHPh\cdot CH\cdot COOH\\ |\quad\quad\quad |\\ NH\cdot N:C\cdot COOH\end{matrix}$, melts at 178° with decomposition, and, on reduction with sodium amalgam, yields *phenylpyrazolidinedicarboxylic acid*, which is being further investigated.

5-Phenylpyrazole-3 : 4-dicarboxylic acid is formed by the oxidation of the pyrazolinedicarboxylic acid with potassium ferricyanide; it is deposited from ether in yellow crystals, melts at 243° with decomposition, is not acted on by potassium permanganate in alkaline solution, and gives the fluorescein reaction.

5-Phenylpyrazole, $C_3N_2H_3Ph$, is prepared by heating the preceding compound, or by distilling silver phenylpyrazolinedicarboxylate in a current of carbonic anhydride; it crystallises in colourless plates melting at 228°. The *silver* salt is sparingly soluble; the *hydrochloride* crystallises in needles melting at 215—218°; the *platinochloride* is orange-red and melts at 287°.

5-Phenylpyrazoline, $NH<\begin{matrix}CHPh\\ N:CH\end{matrix}>CH_2$, is obtained from the hydrochloride as a yellow oil. The *hydrochloride* is prepared by boiling the dicarboxylic acid with hydrochloric acid; the simultaneous formation of hydrazine salts could not be detected; it is colourless and crystalline, melts at 162° with decomposition, reduces copper acetate solution, and, on treatment with bromine, yields 3-phenylpyrazole. The position of the phenyl group in the preceding compounds cannot be regarded as being definitely proved; the mutual attraction of the phenyl and imido-groups renders the formulæ given the more probable.

J. B. T.

Ammonium Derivatives of Azines. By O. FISCHER and E. FRANCK (*Ber.*, **26**, 179—183).—It has previously been shown that ammonium derivatives of the azines may be obtained by the action of alkyl iodides on the azines (Abstr., 1891, 1514), and the present paper gives a detailed account of the compounds obtained.

n-Methylnaphthophenazonium iodide, $C_{10}H_6<\begin{matrix}N\\ NMeI\end{matrix}>C_6H_4$, obtained by heating $\alpha\beta$-naphthophenazine with methyl iodide, diluted with methyl alcohol or ether, under pressure for 10 hours at 130°, crystallises in brownish-red needles, which yield yellow solutions having a greenish-yellow fluorescence. When treated with silver oxide, it yields the corresponding *n-methylphenazonium hydroxide* in red plates, having a metallic lustre; it is somewhat unstable, melts with decom-

position at 175°, and yields reddish-yellow solutions having a brownish-yellow fluorescence. The corresponding *ethyl* derivatives are obtained in a similar manner, the *iodide* forming almost black needles, and melting at 150° with decomposition, and the *hydroxide*, cinnabar-red plates having a greenish shimmer, and melting at 185° when quickly heated.

Phenazine, when treated in a similar manner with methyl iodide and ethyl iodide, yields substances belonging to the group of periodides having the composition $C_{12}H_8N_2MeI_3$ and $C_{12}H_8N_2EtI_3$ respectively; they both form green crystals and yield iodoform with alcohol and sodium carbonate. The corresponding hydroxides could not be obtained pure. H. G. C.

Naphthazines. By O. Fischer and A. Junk (*Ber.*, **26**, 183—187).—As already stated by Fischer and Hepp (Abstr., 1890, 614), α-nitroso-β-naphthylamine, when heated with α-naphthylamine hydrochloride, is converted into asymmetrical αβ-naphthazine,

$$C_{10}H_6\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_{10}H_6;$$

this is purified by repeated crystallisations from benzene or ethyl benzoate, and then melts at 283°; it forms orange-yellow, slender needles, which sublime with simultaneous carbonisation; the *hydrochloride* crystallises in dark red, felted needles. When heated with methyl iodide under pressure, it is converted into the *methiodide*, $C_{22}H_{18}N_2,MeI$, which forms brown needles with a green, metallic shimmer, yields solutions in alcohol and acetic acid having a brown fluorescence, and dissolves in concentrated sulphuric acid with a cornflower-blue colour. The corresponding hydroxide has not been obtained pure.

α-Nitroso-β-naphthylamine and β-naphthylamine yield the symmetrical αβ-naphthazine already described by Mathes (Abstr., 1890, 993), but the yield is very small. The chief product is a new *αβ : ββ-naphthazine*, which crystallises in woolly, orange-yellow needles, melts at 295—296°, and dissolves in concentrated sulphuric acid with a greenish-blue colour. Although its purple-violet solution in acetic acid shows no fluorescence, the benzene and ethyl benzoate solutions have a deep green fluorescence. The *hydrochloride* forms dark brown needles, and the *methiodide* brown needles with a violet shimmer, which yields a non-fluorescent red solution in alcohol and acetic acid.

Symmetrical αβ-naphthazine may be prepared in an analogous manner to naphthophenazine (Abstr., 1887, 1114), by dissolving ββ-dinaphthylnitrosamine in acetic acid and heating for an hour at 60—70°; with methyl iodide, it yields a *methiodide* which crystallises in pale brown needles and dissolves in alcohol or acetic acid, forming a yellow solution with a grass-green fluorescence. H. G. C.

Orthodiamine Derivatives. By O. Fischer (*Ber.*, **26**, 187—204; compare Abstr., 1892, 1472).—When orthamidoparaditolylamine is boiled for half an hour with acetic acid and acetic anhydride, the

acetyl derivative (Abstr., 1891, 434) is not formed, but the corresponding *anhydro-base*, $C_6H_4<\begin{matrix}N(C_7H_7)\\N=CMe\end{matrix}>$; this crystallises in tufts of white needles, and melts at 94—95°; the *platinochloride*,

$$(C_{16}H_{16}N_2)_2,H_2PtCl_6,$$

forms yellow prisms.

When β-phenylorthonaphthylenediamine is oxidised by dry distillation with lead oxide, yellow needles of αβ-naphthophenazine, $C_{10}H_6<\begin{matrix}N\\|\\N\end{matrix}>C_6H_4$, melting at 142°, are obtained. If the amine is boiled with alcoholic potash and carbon bisulphide, a thiocarbamide, $C_{17}H_{12}N_2S$, is formed; this crystallises in flat, colourless needles, melts at a temperature higher than the boiling point of sulphuric acid, dissolves in alkalis, and yields naphthophenazine when distilled with lead oxide.

n-*Phenylmethylorthonaphthylenediamine*, $NHMe\cdot C_{10}H_6\cdot NHPh$, is obtained by heating phenylnaphthylenediamine with methyl iodide in methyl alcohol solution, under pressure at 100°, or by allowing the solution to remain for a long time at the ordinary temperature. It melts at 85°, crystallises in colourless plates, and yields a nitrosamine with nitrous acid. The correspondimg *ethyl* compound, $C_{18}H_{18}N_2$, was prepared in a similar manner; it crystallises in colourless plates or needles, and melts at 71°; its *hydrobromide*, $C_{18}H_{18}N_2,HBr$, forms colourless plates, melting at 221°. With nitrous acid, it yields a *mononitrosoamine*, $NO\cdot NEt\cdot C_{10}H_6\cdot NHPh$, which crystallises in yellowish tables, melts at 145—146°, and gives Liebermann's reaction. With *acetic* anhydride, it yields an *anhydro-base*, $C_{10}H_6<\begin{matrix}NEt\\NPh\end{matrix}>CMe\cdot OH$, which melts at 197—198°, and crystallises in short prisms. When heated at 100° with benzaldehyde, it yields a dihydroimidazole, $C_{10}H_6<\begin{matrix}NEt\\NPh\end{matrix}>CHPh$, which crystallises in colourless needles, melts at 108°, and is decomposed into its constituents on treating it with mineral acids.

Diphenyldihydrotoluquinoxaline, $C_6H_3Me<\begin{matrix}NH\cdot CHPh\\|\\N=CPh\end{matrix}$, melting at 143°, is obtained in yellow needles on heating 1 : 3 : 4-tolyleneorthodiamine with benzoïn at 180° under pressure, in addition to some of the diphenyltoluquinoxaline of Hinsberg (Abstr., 1884, 1052), melting at 111°. The iron salt of the latter is readily formed when the dihydro-compound is oxidised by warming its alcoholic solution with ferric chloride.

Diphenyldihydronaphthaquinoxaline, is obtained in a similar manner from αβ-naphthylenediamine, together with some of the diphenylnaphthaquinoxaline melting at 147° prepared by Lawson (Abstr., 1885, 1238). It is converted into the latter substance by oxidation with ferric chloride. It forms yellow crystals, and melts at 172°.

β-Ethylnaphthylenediamine can be prepared in the following manner:—β-Ethylnaphthylamine is converted into the *benzeneazo*-compound, $NHEt\cdot C_{10}H_6\cdot N_2Ph$, which crystallises in dark red needles,

melting at 105°; or, by treatment with paradiazobenzenesulphonic acid, into the compound $NHEt{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$. The latter, when reduced with zinc-dust and acetic acid, yields the diamine as a viscid, unstable oil; the *hydrochloride* forms colourless plates which easily turn red; the *platinochloride*, $(C_{12}H_{14}N_2)_2,H_2PtCl_6$, is a yellow, crystalline powder. With salicylaldehyde it yields an *anhydro-base*, $C_{10}H_6<^{—C}_{NEt}>C{\cdot}C_6H_4{\cdot}OH$, crystallising in yellowish-white prisms, and melting at 133°. With paranitrobenzaldehyde, an analogous *anhydro-base* is obtained in yellow needles melting at 225°.

1 : 3 : 4-*Methyltolylenediamine* was prepared by Gattermann's method (Abstr., 1885, 975). It is a very unstable substance; its *hydrochloride*, $C_9H_{12}N_2,HCl$, forms colourless plates melting at 175—180°; the *sulphate*, hygroscopic, deliquescent, colourless or reddish needles; the *picrate*, $C_9H_{12}N_2,C_6H_3N_3O_7$, small, yellow crystals melting at 164°; and the *oxalate*, $C_9H_{12}N_2,C_2H_2O_4$, white needles melting at 124°. When boiled with formic acid, it yields *methenylpara-n-methyltolylenediamine*, $C_6H_3Me<^{—N}_{NMe}>CH$ [Me : N : NMe = 1 : 3 : 4], as colourless needles melting at 94°. This is isomeric with the substance obtained by O. Fischer (Abstr., 1889, 731) from methenyltolyleneamidine and methyl iodide; Fischer's compound must have been $C_6H_3Me<^{NMe}_{—N}>CH$ [Me : NMe : N = 1 : 3 : 4]. The *ethenyl* compound, $C_{10}H_{12}N_2$, was prepared in a similar manner, using acetic anhydride; it forms colourless needles melting at 142°, and is identical with the substance obtained by Niementowski (Abstr., 1887, 937) by reducing methylmetanitroparacetotoluidide with carbon bisulphide; the diamine yields a *thiocarbamide*, $C_6H_3Me<^{NH}_{NMe}>CS$ or $C_6H_3Me<^{—N}_{NMe}>C{\cdot}SH$; this forms white needles, melts at 194°, and dissolves in alkalis. With benzaldehyde, the diamine yields *n-methylbenzenyltolyleneamidine*, $C_6H_3Me<^{—N}_{NMe}>CPh$, as colourless crystals melting at 126—127°; the *platinochloride*, $(C_{15}H_{14}N_2)_2,H_2PtCl_6$, forms brilliant, yellow needles melting above 300°. Orthonitrobenzaldehyde yields an analogous compound, $C_{15}H_{13}N_3O_2$, as yellow crystals melting at 152—153°. Paranitrobenzaldehyde also yields an analogous compound, $C_{15}H_{13}N_3O_2$, crystallising in brown needles. Salicylaldehyde yields a compound, $C_{15}H_{14}N_2O$, melting at 180°, and crystallising in white needles. Benzoïn yields *n-methyldiphenyltoluidohydroquinoxaline*, $C_6H_3Me<^{N=CPh}_{NMe{\cdot}CHPh}$, melting at 135°. This, when oxidised with ferric chloride, yields a yellow iron salt melting at 118°, but the base liberated from this could be obtained only as an uncrystallisable oil.

Parethylorthotolylenediamine, $C_6H_3Me(NHEt){\cdot}NH_2$ [= 1 : 4 : 3], melting at 55°, has already been prepared by Gattermann (Abstr., 1885, 975). The *hydrochloride*, $C_9H_{14}N_2,HCl$, is a white substance melting at 176°; the *oxalate*, $(C_9H_{14}N_2)_2,C_2H_2O_4$, forms white needles

melting at 151°. With carbon bisulphide, it yields a thiocarbamide, $C_6H_3Me<^{-N}_{NEt}>C\cdot SH$, which melts at 139°, crystallises in white, asbestos-like needles, and is soluble in alkalis. With acetic anhydride, it yields *ethenylethyltolylenediamine*, $C_6H_3Me<^{-N}_{NEt}>CMe$, in colourless crystals melting at 165—166°. The isomeric substance melting at 93°, obtained by Hübner (Abstr., 1882, 503) by ethylating ethenyltoyleneamidine, must have been $C_6H_3Me<^{NEt}_{-N}>CMe$ [Me : NEt : N = 1 : 3 : 4]. Benzaldehyde with the diamine yields the compound $C_6H_3Me<^{-N}_{NEt}>CPh$, as yellow needles; its *platinochloride*, $(C_{16}H_{16}N_2)_2,H_2PtCl_6$, forms yellow plates. Orthonitrobenzaldehyde yields an analogous compound, $C_{16}H_{15}N_3O_2$, as yellow crystals melting at 170°. Paranitrobenzaldehyde yields a benzylidene compound $NHEt\cdot C_6H_3Me\cdot N:CH\cdot C_6H_4\cdot NO_2$, as red needles; these, when crystallised from alcohol, become converted, by gradual oxidation, into yellow needles, consisting of a compound, $C_{16}H_{15}N_3O_2$, corresponding with that obtained from orthonitrobenzaldehyde; it melts at 176°. Salicylaldehyde also yields a similar compound, $NHEt\cdot C_6H_3Me\cdot N:CH\cdot C_6H_4\cdot OH$, as yellow needles melting at 78°, and convertible, by oxidation with mercury oxide, into the anhydro-base; this forms colourless crystals, and melts at 112—116°. With benzoïn, the diamine yields n-*ethyldiphenyldihydrotoluquinoxaline*,

$$C_6H_3Me<^{N=CPh}_{NEt\cdot CHPh'}$$

in yellow crystals melting at 129°. When oxidised with ferric chloride, this substance yields an iron salt which crystallises in yellow needles, and melts at 155—160°. The base liberated from the iron salt was an uncrystallisable oil. C. F. B.

Constitution of Nicotine. By A. Pinner (*Ber.*, **26**, 292—305; see also Abstr., 1892, 1497).—A further examination of the two compounds obtained by the action of bromine on nicotine shows that they have the compositions $C_{10}H_{10}N_2Br_2O$ and $C_{10}H_8N_2Br_2O_2$. The author names these compounds dibromocotinine and dibromoticonine respectively.

Dibromocotinine is obtained as perbromide, $C_{10}H_{10}N_2Br_2O,HBr_3$, by adding bromine to an aqueous solution of nicotine hydrobromide. The free base is best prepared by treating the perbromide with aqueous sulphurous acid, and then adding potassium carbonate. It crystallises from dilute alcohol in beautiful colourless prisms, melts under boiling water, but when dry it melts at 125°. The *hydrochloride* crystallises in needles, and turns blue on heating. The *methiodide*, $C_{10}H_{10}N_2Br_2O,MeI$, crystallises in beautiful prisms, and melts at 175° with decomposition. Neither a benzoyl nor acetyl compound could be obtained. Hydroxylamine and phenylhydrazine are without action at low temperatures, and at higher temperatures complete decomposition ensues. When heated with sulphurous and sulphuric

acids at 130—140°, or with sodium sulphite and fuming hydrochloric acid at 150°, it yields methylamine, oxalic acid, and β-methyl pyridyl ketone. The latter yields a platinochloride, C_7NH_7O,H_2PtCl_6, which crystallises in flat, yellowish-red needles, and melts at 193° with decomposition.

Cotinine, $C_{10}N_2H_{12}O$, is obtained, together with a small quantity of nicotine, by reducing the above perbromide with zinc-dust and hydrochloric acid. It melts at 50°, distils as a colourless oil at 330° under the ordinary pressure, and at 250° under 150 mm. It is extremely stable, and is not altered by heating with baryta or with hydrochloric acid at 180°. The *platinochloride* crystallises in beautiful, yellowish-red prisms, and melts at 220° with carbonisation.

Dibromoticonine.—The *hydrochloride* crystallises in colourless needles, and blackens above 200° without melting. The *platinochloride* crystallises in yellow prisms, begins to darken at 230°, sinters at 240°, and does not melt at 250°. The *picrate* crystallises in small, yellow needles, turns brown at 220°, and melts at 235° with violent decomposition. Dibromoticonine, when reduced in cold alkaline solution with zinc-dust, yields monobromoticonine; in a warm alkaline solution, however, it yields methylamine and pyridyl-βγ-dihydroxybutyric acid, $C_5NH_4\cdot[CH\cdot OH]_2\cdot CH_2\cdot COOH$. When heated with barium hydroxide in a sealed tube at 100,° it yields methylamine, nicotinic acid, and malonic acid.

Bromoticonine, $C_{10}H_9N_2BrO_2$, is obtained in small rhombohedra, and is easily soluble in alcohol. The *hydrochloride* forms small prismatic crystals, and when heated decomposes without melting.

In consideration of the above results, the author assigns to dibromocotinine the constitution $C_5NH_4\cdot CBr\cdot CH_2 > NMe\cdot CO > CHBr$, and to dibromoticonine the constitution $C_5NH_4\cdot CBr\cdot CO > NMe\cdot CO > CHBr$. And thence deduces for nicotine the constitution $C_5NH_4\cdot CH\cdot CH_2 > NMe\cdot CH_2 > CH_2$.

E. C. R.

Oxidation of Strychnine. By J. Tafel (*Ber.*, **26**, 333—335; compare Abstr., 1890, 1447; 1891, 1262; 1892, 1012).—By successive treatment of strychnine with dilute and concentrated nitric acid, the author has succeeded in obtaining a series of crystalline, well characterised acids, one of which has the composition $C_{10}H_5N_3O_8$, and contains the carboxyl group, two nitro-groups, and two hydroxyl groups; its formula may, therefore, be resolved as follows: $C_9H_2N(NO_2)_2(OH)_2\cdot COOH$. Such an acid must in all probability be a derivative of quinoline or isoquinoline, and it is hoped that the further examination of this and the other acids mentioned above will lead to important conclusions with regard to the constitution of strychnine.

H. G. C.

Pseudopelletierine. By G. Ciamician and P. Silber (*Ber.*, **26**, 156—159; compare Abstr., 1892, 1110).—*Pseudopelletierine oxime*, $C_9H_{15}N_2O$, is formed on treating an aqueous solution of the base

with hydroxylamine; it crystallises in colourless, rhombic plates melting at 128—129°. The *hydrochloride*, $C_9H_{16}N_2O,HCl$, forms well-defined crystals, and volatilises when heated, but without melting.

A *base*, which seems to have the composition $C_9H_{17}NO$, is produced, together with a very small quantity of a crystalline substance melting at 240—260°, when pseudopelletierine is reduced with sodium amalgam in aqueous solution; it can be isolated in the form of its *aurochloride*, $C_9H_{17}NO,HAuCl_4$, which crystallises in yellow needles melting at 203°.

When pseudopelletierine methiodide (*loc. cit.*) is heated with a solution of barium hydroxide, it is decomposed into dimethylamine and a colourless oil of the composition $C_8H_{10}O$, which boils at 197—198°; the latter is possibly a dihydroacetophenone, as, on oxidation with alkaline potassium permanganate, it yields phenylglyoxylic acid, and a small quantity of another acid which, however, was not obtained in a state of purity.

A compound of the composition $C_9H_{12}BrNO_2$ is formed when pseudopelletierine hydrobromide is treated with excess of bromine; it crystallises in long needles, melts at 207°, and is soluble in acids and alkalis, but only sparingly in hot water. F. S. K.

Amyloïd Substance. By N. P. Krawkow (*Bied. Centr.*, **21**, 753—754; from *Centr. Med., Wiss.*, 1892, 145—148).—Amyloïd gives the characteristic carbohydrate reaction with iodine, notwithstanding its proteïd nature. It differs from all other known products of degeneration in not being present in the organism in any phase of the physiological life, and is therefore looked on as a pathological product. It is now shown that chitin, $C_{60}H_{100}N_8O_{38} + nH_2O$ (which according to Sundwick is the amine derivative of a carbohydrate, $C_{60}H_{100}O_{50}$), which occurs very extensively in the animal kingdom, gives the characteristic reactions of amyloïd.

Chitin was prepared by extracting crab's shell with dilute hydrochloric acid, boiling with 5 per cent. aqueous potash, decolorising with permanganate, and after making slightly acid, extracting with alcohol and ether. The colourless plates so obtained gave an intense red-brown coloration with iodine, which changed to violet on the addition of sulphuric acid or zinc chloride. Methyl-violet colours chitin violet-red or violet. Chitin plates kept in the abdominal cavity of a dog for two or three weeks gave a more distinct reaction with methyl-violet; keeping in the lymph cavity of a frog had no effect. The examination of several chitin formations (of crabs, cockroaches, spiders, &c.), showed that the chitin is not everywhere the same. The horny, inner wall of a bird's crop, which is also possibly chitin, gave the iodine reaction and (very feebly) the methyl-violet reaction. Chitin is produced in normal life, not only in the lower, but also in some higher animals. N. H. M.

Organic Chemistry.

Combination of Cuprous Cyanide with Alkali Cyanides. By E. Fleurent (*Compt. rend.*, **116**, 190—191).—The colourless solution from which the blue and green ammoniocupric compounds previously described (Abstr., 1892, 1065) have separated, quickly deposits plates with a micaceous lustre, and afterwards, when the solution has become concentrated by spontaneous evaporation, prismatic crystals separate. The micaceous plates are *diammoniocuprous diammonium cyanide;* this is insoluble in cold water, but is decomposed by boiling water with evolution of ammonia and precipitation of cuprous cyanide, and by acids with liberation of hydrogen cyanide and separation of cuprous cyanide. It is soluble in ammonia, and the solution rapidly becomes blue. When heated, the compound decomposes with liberation of water, ammonia, and ammonium cyanide, a residue of cuprous cyanide and metallic copper being left.

The prismatic crystals are *potassium cuprous cyanide*, $Cu_2Cy_2,2KCy$, and consist of rhombic prisms truncated by pyramids. They are insoluble in, but are partially decomposed by, cold water, and are decomposed by boiling water, yielding cuprous and potassium cyanides. The compound dissolves in ammonia, forming a blue solution, and is decomposed by acids and by the action of heat.

C. H. B.

Tribromacetonitrile. By C. Broche (*J. pr. Chem.* [2], **47**, 304).—*Tribromacetonitrile*, $CBr_3{\cdot}CN$, is obtained by distilling tribromacetamide with phosphorus pentoxide; it is a red, heavy, refractive liquid, boils undecomposed at 170°, and has the characteristic nitrile odour. Hydrogen bromide does not polymerise this nitrile (compare Tscherwen-Iwanoff, Abstr., 1891, 1332); by saturating it with hydrogen chloride it is solidified, after some days, into a compound which shows a molecular weight by the cryoscopic method corresponding with $(CBr_3{\cdot}CN)_3$; this crystallises in long, slender needles, and melts at 129—130°. The matter is being further investigated.

A. G. B.

Reactions of Ferric Salts with Thiocyanates. By J. H. Gladstone (*Chem. News*, **67**, 1—3).—The author comments on H. M. Vernon's communication (this vol., i, 122), draws attention to certain misconceptions of his own work on the subject contained therein, indicates some probable causes of the variation of certain of that author's views from his own views, and finally expresses the opinion that, without discussing the theoretical conclusions, it would seem that Vernon's experiments are not only in accordance with his own views, but furnish some additional arguments in their favour. In the paper under comment, there is an assumption "that ferric chloride and potassic thiocyanate, in equivalent quantities, react almost completely at infinite concentration to form ferric thio-

cyanate;" this is apparently based on a comparison made with ferric thiocyanate prepared by decomposing barium thiocyanate by ferric sulphate. It is now shown that the ferric thiocyanate prepared in this manner is impure and not suitable for such comparison; the author is therefore still of opinion that there is no reason to suppose that in the mixture referred to, the ordinary law of reciprocal decomposition and the usual effect of increased mass do not hold good. Then, with reference to the effect of change of temperature on these reactions, the author points out that he showed, in his paper, "On the Effect of Heat on the Colour of Salts in Solution," (*Phil. Mag.*, 1857), that ferric chloride passes from orange to a deep and almost pure red. He now demonstrates that the amount of change varies greatly with the proportion of water present, and the length of time during which the heating is continued. Thus, in a 3·8 per cent. solution, the depth of colour was about doubled, whilst in a 0·06 per cent. solution, it was increased fourfold when heated from 20° to 60°; again a twentyfold increase of colour is observed when 1 equivalent of potassium thiocyanate is added to a solution containing 100 equivalents of ferric chloride at the ordinary temperature, but when the two are compared at 60°, the increase is not nearly so great. A weakening in colour on heating is also observed in a solution of the impure ferric thiocyanate prepared from barium thiocyanate and ferric sulphate, and in a solution containing 1 equivalent of ferric chloride to 100 equivalents of potassium thiocyanate; in fact the reduction in colour in this last case by heating from 20° to 60° amounted to 50 per cent. This result the author regards as curious, as it indicates that the action of increased temperature on ferric thiocyanate is analogous to that of increased dilution, whereas, in all solutions of coloured salts examined by him in 1857, the reverse was the case.

D. A. L.

Reactions of Ferric Salts with Thiocyanates. By H. M. Vernon (*Chem. News*, **67**, 66; compare this vol., i, 122, and preceding abstract).—Referring to the comments in the preceding abstract, the author points out that, in the ferric chloride and potassium thiocyanate reaction, there are present in solution potassium chloride and ferric thiocyanate, and that the barium thiocyanate and ferric sulphate experiment merely shows that the removal of one reacting salt from the solution produced practically no increase of colour. The author is, moreover, of opinion that only a small part of the change on heating ferric thiocyanate solutions is due to ferric chloride, and therefore, that the ferric thiocyanate solutions, under suitable conditions, increase in colour effect on heating, and so conform with the observation made by Gladstone in 1857 on solutions of other coloured salts.

D. A. L.

Thiocyanates of certain Chromammonium Compounds. By O. Nordenskjöld (*Zeit. anorg. Chem.*, **1**, 126—143).—Morland (this Journal, **13**, 252) obtained a compound by the action of potassium dichromate on fused potassium thiocyanate; it was subsequently examined by Reinecke (*Annalen*, **126**, 113). The author finds that it is best prepared by heating ammonium thiocyanate to

incipient fusion, and dropping in one-third its weight of ammonium dichromate; it is also obtained by adding 25 per cent. ammonia to a fused mixture of chromium thiocyanate and ammonium thiocyanate. The results described below show that it is an ammonium salt; its composition is represented by the formula $Cr(NH_3)_2(SCN)_4NH_4$. It forms small, red crystals, is fairly stable towards acids, but is decomposed by alkalis; the corresponding *potassium* salt, $Cr(NH_3)_2(SCN)_4K$, is obtained by adding potassium chloride to its solution. Both salts combine with 1 atom of iodine. The *barium*, *ferric*, *mercuric*, *silver*, *aniline*, and *piperidine* salts were also prepared. A reddish-yellow *compound*, $Cr(NH_3)_2(SCN)_3(HgS)_6$, separates when the mercuric salt is treated with hydrogen sulphide, whilst the *acid*, $Cr(NH_3)_2(SCN)_4H + H_2O$, is isolated from the filtrate, and is also obtained by decomposing the barium salt with sulphuric acid; it commences to decompose at 80°.

When the above-described ammonium salt is boiled with hydrogen peroxide, hydrogen cyanide is evolved and a *compound*,

$$Cr(NH_3)_2(SCN)_3 + 2H_2O,$$

crystallising in large, purple, six-sided tables is obtained. It is only decomposed when treated with concentrated alkali, and when aniline, piperidine, or ethylenediamine is added to its solution, 1 or 2 mols. of water are displaced by residues of these bases.

A. R. L.

Hydrates of Alcohols. By R. de Forcrand (*Ann. Chim. Phys.* [6], **27**, 525—549).—From numerous measurements of the heat generated on mixing aqueous solutions of isopropyl alcohol of different concentrations with a large volume of water, the author concludes that the alcohol forms two hydrates, of the composition $2C_3H_8O,H_2O$ and $C_3H_8O,4H_2O$ respectively, but no evidence of the existence of other hydrates was obtained. From an examination of the results obtained by Dupré and Page, it would seem that methyl and ethyl alcohols form hydrates of the composition $CH_4O,2H_2O$ and $C_2H_6O,6H_2O$ respectively.

F. S. K.

Adonitol, a new Pentitol. By E. Fischer (*Ber.*, **26**, 633—639).—The annual report for 1892 issued by Merck, of Darmstadt, contains a description of a crystalline pentahydric alcohol obtained from *Adonis vernalis*, and named *adonitol;* this alcohol has now been examined by the author, who gives in the present paper the results of his own experiments, as well as Merck's description of the properties of the substance.

Adonitol, $C_5H_{12}O_5$, is very readily soluble in water, from which it crystallises in large, transparent prisms; the solution has at first a sweet taste, but this impression soon passes away, the tongue being left with a certain dull sensation; it is insoluble in ether and light petroleum, but dissolves freely in hot alcohol, being deposited from the solution on cooling in colourless needles. It begins to sinter at 99°, melts at 102°, and undergoes a slight increase in weight on prolonged heating at 105—115°, probably the result of absorption of oxygen; it does not reduce Fehling's solution, gives no coloration with aqueous alkalis, and dissolves in warm concentrated sulphuric

acid yielding a colourless solution; it is optically inactive, and has no specific physiological action.

When adonitol is oxidised with a cold dilute solution of sodium hypobromite, it is converted into a sugar, which, however, was not isolated. The *osazone*, $C_5H_8O_3(N_2HPh)_2$, prepared by treating the solution of this sugar with phenylhydrazine and acetic acid in the usual manner, separates from boiling water in yellow crystals, begins to sinter at 140°, and melts completely at 147°; it is very similar in properties to l.-arabinosazone, and, as will be shown below, it is very closely related to this substance.

Dibenzyladonitol, $C_5H_8O_3(CHPh)_2$, is formed when adonitol is treated with benzaldehyde and 50 per cent. sulphuric acid; it separates from hot alcohol in slender needles, melts at 164—165° (uncorr.), is only very sparingly soluble in hot water, and is decomposed into adonitol and benzaldehyde by boiling 5 per cent. sulphuric acid.

The results described above prove that adonitol is isomeric with l.-arabitol and xylitol, the only pentahydric alcohols known: xylitol has not yet been obtained in crystals, but adonitol and l.-arabitol are not only similar in crystalline form and in solubility, but they have also the same melting point, and are both optically inactive in aqueous solution. Although so similar in general properties that they might be supposed to be identical, their aqueous solutions show a different optical behaviour in presence of borax, that of arabitol becoming fairly strongly lævorotatory, that of adonitol remaining inactive. The inference that adonitol is the inactive racemic modification of arabitol, although apparently well founded, is, however, negatived by the fact that adonitol yields a crystalline, whereas arabitol gives an oily, benzal derivative. It would seem, therefore, that adonitol is not directly related to either of the known isomerides; assuming, further, that it contains a normal chain of carbon atoms, its configuration must be represented by the formula

$$\begin{array}{l} OH\cdot CH_2\cdot \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} \cdot CH_2\cdot OH, \end{array}$$

that is to say, it is the alcohol of ribose.

This view was proved to be correct; the pentahydric alcohol obtained by reducing ribonic lactone (Abstr., 1892, 437) with sodium amalgam is identical with adonitol.

Adonitol is the first pentitol that has been discovered in the vegetable kingdom, and the very fact of its occurrence renders it probable that ribose or its optical isomeride will also be met with in nature; judging from the experience gained in the reduction of mucic acid, there can be no doubt that all adonitol derivatives the molecules of which are asymmetric will be racemic modifications, as, for example, is so in the case of the osazone, which must be regarded as the racemic modification of arabinosazone. F. S. K.

Dextrose. By A. Wohl (*Ber.*, **26**, 730—744).—The oxime of dextrose, when treated with acetic anhydride, yields an acetyl derivative from which hydrogen cyanide can be eliminated, and on hydrolysis of the resulting compound a pentose is obtained. By repeating

this operation, the author hopes to prepare the series of compounds from dextrose to formaldehyde.

The *glucose oxime* is obtained as follows:—A solution of sodium in absolute alcohol is added to an aqueous solution of hydroxylamine hydrochloride in such proportions that phenolphthalein is no longer turned red. The mixture is filtered, heated to boiling, and then finely-powdered pure dextrose is added. On allowing the mixture to remain in a warm place for a few days, pure crystals of the oxime are deposited. It melts at 137·5°, and yields a stable hexacetyl derivative (m. p. 109—110°) and an unstable pentacetyl derivative.

Pentacetylglucononitrile is obtained by warming the oxime with fused sodium acetate and acetic anhydride: the product is poured into cold water, alkali added until the mixture is only faintly acid, and the precipitate crystallised from alcohol. It melts at 80—81°, and forms hemihedral crystals belonging to the rhombic system, $a : b : c = 0{\cdot}66817 : 1 : 0{\cdot}61841$. When hydrolysed with hydrochloric acid and treated with phenylhydrazine, it yields gluconic phenylhydrazide, m. p. 195—197°. When warmed with potassium hydroxide or treated with silver nitrate or ammoniacal silver solution, hydrogen cyanide is eliminated, and a pentose derivative is obtained. The alcoholic solution of the nitrile is treated with a solution of silver oxide in ammonia from which the excess of ammonia has been removed, and after the mixture has remained for some hours, the filtrate is freed from silver by means of hydrogen sulphide, and evaporated to a syrup. On hydrolysis, this syrup yields a mixture containing the pentose, which, however, is not obtained crystalline by this method. The *pentosazone* is, however, easily obtained from the mixture, and melts at 159—160°.

An *acetamide derivative* of the pentose,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH(NHAc)_2,$$

is formed when the syrup obtained by the elimination of hydrogen cyanide from the above nitrile is allowed to remain two days with 30 per cent. ammonia. It may be prepared directly from the nitrile by allowing it to remain two days with silver oxide and excess of ammonia, and then heating the mixture on the water-bath, and, after driving off the ammonia with a current of air, concentrating the filtrate under diminished pressure. It crystallises in slender, white needles, has a sweet taste, is soluble in 25 parts of hot and 100 parts of cold 90 per cent. alcohol, and has a specific rotatory power $[\alpha]_D^{20} = -9{\cdot}5°$. When heated with dilute hydrochloric or sulphuric acid on the water-bath, it yields the pentose and acetamide.

The pentose *d.-arabinose* is obtained by heating the preceding compound (10 grams) with 50 c.c. of 6N sulphuric acid for 15 minutes on the water-bath. The cold solution is extracted with ether, which removes the acetic acid produced during the reaction. The acid solution is then exactly neutralised with barium hydroxide, and the filtrate, after boiling in a porcelain dish to remove the ammonia, is evaporated in a vacuum or on the water-bath to a syrup. d.-Arabinose tastes sweet, and crystallises in long, colourless prisms,

in the rhombic system, $a : b : c = 0{\cdot}66810 : 1 : 0{\cdot}48989$. The specific rotatory power is $[\alpha]_D^{20} = -104{\cdot}1°$. It yields furfuraldehyde with strong acids, is coloured yellow by alkalis, reduces Fehling's solution, and yields the osazone $C_5H_8O_3(N_2HPh)_2$ with phenylhydrazine, and the hydrazone $C_5H_{10}O_4{\cdot}N_2H{\cdot}C_6H_4Br$ with bromophenylhydrazine.

i.-Arabinose is obtained by mixing solutions of the optical antipodes, and crystallises in microscopic needles. The *osazone* melts at 163°.

l.-Arabinose, when treated in a similar way to that described above for dextrose, is converted into a tetrose derivative.

l.-Arabinose oxime melts at 132—133°, and yields hydrocyanic acid when melted with an alkali. *Tetracetylarabinonitrile* melts at 117—118°, and, when treated with ammoniacal silver solution, yields a tetrose derivative. E. C. R.

Xylose. By W. E. Stone and W. H. Test (*Amer. Chem. J.*, **15**, 195—197).—Xylose is conveniently obtained from the alkaline waste liquor which results from the digestion of straw with lime at a high temperature in the paper manufacture. The liquor contains, among other compounds, xylan, the mother substance of xylose, and this is precipitated by alcohol from the concentrated and acidified liquor, and purified by repeated solution in water and reprecipitation with alcohol. The yield of crude xylan is about 1 per cent. It still contains, however, a considerable amount of lime salts, and yields, on distillation with hydrochloric acid, about 46 per cent. of furfuraldehyde, as determined by titration with phenylhydrazine. The xylan is hydrolysed with dilute sulphuric acid, and the resulting solution of xylose neutralised, evaporated to a syrup, and extracted with alcohol. The alcoholic extract yields a syrup of xylose, which soon crystallises, and is identified by its specific rotatory power $[\alpha]_D = 18{\cdot}4°$, and the melting point, 158°, of its lævorotatory osazone. The straw liquor may be hydrolysed directly without the intermediate separation of the xylan, and with equally good results. The authors confirm the observations of Tollens and Parcus (Abstr., 1890, 1084) as to the multirotation of xylose. The specific rotatory power in aqueous solution diminished in the course of three hours from $[\alpha]_D = 71{\cdot}65°$ to $18{\cdot}95°$, and eventually became constant at 18·40°.

Jn. W.

Gum Arabic. By A. Béchamp (*Bull. Soc. Chim.* [3], **7**, 587—600).—The so-called nitro-derivatives of arabin, like those of starch and cellulose, are nitrates. Arabin mononitrate has a rotatory power in alcoholic solution $[\alpha]_j = 23{\cdot}2—28{\cdot}2°$, and arabin dinitrate a rotatory power $[\alpha]_j = 22{\cdot}56°$, whilst arabin itself is lævorotatory, the author having previously fixed its rotatory power at about −36°. In view, however, of the somewhat conflicting statements of other chemists, he has re-determined the constant.

The raw material employed was Senegal gum, which was dried at 130°. Arabin prepared from the latter, either by treatment with hydrochloric acid (Fremy's method) or with sodium hydroxide, exhibits a low rotation when the action of these reagents is protracted. The following method appears to be the most satisfactory:

—Glacial acetic acid is added to a thick mulcilage of the gum, the filtered liquid mixed with a larger quantity of glacial acetic acid, and the precipitate collected and washed with fresh quantities of the same acid; it is then redissolved in water, precipitated with a large excess of alcohol, collected, and dried over concentrated sulphuric acid. The arabin thus prepared contains 0·5 per cent. of ash, and has a rotatory power $[\alpha]_j = -35°$. After being heated for some time at 130°, it gives a lower rotation and dissolves in water with a yellow colour. An aqueous solution containing 5—7 per cent. may be mixed with an equal volume of alcohol of 94° without precipitation; the whole of the arabin is, however, precipitated on the addition of a small quantity of ammonium acetate. The author shows that a solution of the gum itself is lævorotatory, like that of the arabin, and solutions of both give a bluish precipitate with Fehling's solution, which dissolves on heating. A solution of arabin becomes dextrorotatory on being heated in a sealed tube at 160°; the product reduces Fehling's solution, and its acid reaction becomes much stronger.

When to a mulcilage of the gum three-fourths the weight of ordinary nitric acid is added in the cold, a similar effect is observed to that produced by hydrochloric or sulphuric acid, namely, the lævorotation becomes a dextrorotation. If, however, the gum is dissolved in a mixture of nitric acid (36° B., 3 parts) and water (1 part), and the solution heated, mucic acid (12—15 per cent.) is formed, the filtrate being lævorotatory. The last-mentioned rotation diminishes, however, on continuing the action, and oxalic acid is produced; the author is therefore inclined to agree with Dubrunfaut, that gum contains both dextro- and lævo-components. A. R. L.

Oxycellulose and Bornesitol. By E. R. Flint and B. Tollens (*Annalen*, **272**, 288—290).—Analyses of fresh preparations of oxycellulose have given results agreeing very closely with those obtained by Sacc, and moderately well with those of Lindsey and Tollens (Abstr., 1892, 827) and of Cross and Bevan (Trans., 1883, 22); oxycellulose does not yield methylic iodide when heated with hydriodic acid, and, judging from its reactions, it would seem to contain aldehyde groups.

A yellowish, crystalline compound obtained from the water used in washing caoutchouc was purified and examined by the authors, and found to be bornesitol, or methylinositol, $C_7H_{14}O_6$; it melted at 199—203°, had a specific rotatory power $[\alpha]_D = +31·16°$, and gave, on treatment with hydriodic acid, a quantity of methylic iodide corresponding with the presence of one methoxy-group. F. S. K.

Explosive Nitrates from the Jute Fibre. By C. F. Cross and E. J. Bevan (*J. Soc. Chem. Ind.*, **11**, 214—215).—The authors criticise a communication by Müllhäuser (*Dingl. polyt. J.*, **283**, 88) on the jute fibre as a raw material for guncotton, which they consider to lack in novelty, most of the facts having been previously described by them (Trans., 1889, 202). D. B.

Chlorine Derivatives of Propylamines, Benzylamines, Aniline, and Paratoluidine. By A. Berg (*Compt. rend.*, **116**, 327—329).—The author uses the terms chloramine and dichloramine to distinguish those compounds in which the halogen replaces the hydrogen in the amido-group, and not in the hydrocarbon group.

Propylchloramine, $NHPrCl$, is obtained by mixing solutions of propylamine hydrochloride and sodium hypochlorite. It is a colourless liquid with a very piquant odour; sp. gr. at 0° = 1·021, but at 15° it is lighter than water at the same temperature. It does not solidify at −50°, and cannot be distilled, because it decomposes very rapidly when gently heated. Decomposition takes place after a little time, even at the ordinary temperature. With sulphuric acid, it yields propylamine and the dichlor-derivative.

Propyldichloramine, $NPrCl_2$, is easily obtained by the method that Tcherniac employed for the preparation of ethyldichloramine. It is a greenish-yellow liquid, with an odour similar to that of other dichloro-derivatives. It does not solidify at −50°, and boils without decomposition at 117° under a pressure of 760 mm.; sp. gr. at 0° = 1·177.

Dipropylchloramine, NPr_2Cl, is obtained by the action of sodium hypochlorite on dipropylamine hydrochloride. It is a colourless, oily liquid, insoluble in water, and decomposes slowly with precipitation of crystals; sp. gr. at 0° = 0·923. It boils at 143° under a pressure of 771 mm., and when treated with alcoholic soda, yields a base that seems to be propylpropylidenamine. When mixed with an alcoholic solution of potassium cyanide, a reaction takes place at the ordinary temperature with development of heat, the product being dipropylcyanamide, identical with that obtained by Chancel by another method (following abstract).

Benzylchloramine, $C_7H_7{\cdot}NHCl$, is obtained in a similar manner. It is a colourless, very unstable liquid, which decomposes very rapidly with deposition of crystals and evolution of thick, white fumes.

Benzyldichloramine, $C_7H_7{\cdot}NCl_2$, cannot be obtained by the reaction used by Tcherniac in the case of ethyldichloramine, but is easily obtained by treating rapidly washed benzylchloramine first with dilute sulphuric acid and then with acid gradually increasing in concentration until it reaches 50 to 60 per cent. Benzyldichloramine is a greenish-yellow liquid with a chlorous odour; sp. gr. at 0° = 1·282. When cooled, it solidifies to greenish-yellow, striated prisms which melt at −11·5°; it cannot be distilled, even in a vacuum.

Dibenzylchloramine, $N(C_7H_7)_2Cl$, is obtained by the action of sodium hypochlorite on dibenzylamine hydrochloride. It crystallises from ether in large, lozenge-shaped crystals which seem to be flattened rhombohedra, and has an agreeable odour, recalling that of oil of bitter almonds, and only slightly chlorous. It is insoluble in water, and only slightly soluble in cold alcohol of 93°, but the solubility in the latter increases very rapidly as the temperature rises, the weight dissolved by 100 parts of alcohol being as follows:—

16°.	34°.	44°.	47·5°.	53°.
3·20	43·88	97·03	164·80	493·60

Dibenzylchloramine melts at 56°, and, if heated rapidly, deflagrates vigorously at 150°; if heated more gradually, deflagration takes place at a lower temperature. At the ordinary temperature, decomposition takes place slowly, and the crystals become partially insoluble in ether. With potassium cyanide, dibenzylcyanamide is formed.

Aniline and paratoluidine yield similar products, which are extremely unstable and deflagrate rapidly a few minutes after the solvent (ether or ethylic chloride) has evaporated. C. H. B.

Dipropylcyanamide and Dipropylcarbodiimide. By F. Chancel (*Compt. rend.*, **116**, 329—330).—*Dipropylcyanamide* is obtained by adding bromine water gradually to a saturated aqueous solution of dipropylamine containing half a molecular proportion of potassium cyanide, until the liquid is neutral: $2NHPr_2 + KCN + Br_2 = NPr_2{\cdot}CN + NHPr_2,HBr + KBr$. It is a mobile liquid, with a burning taste and an aromatic odour, and boils at 107° under a pressure of 21 mm. and at 220° under 770 mm.; sp. gr. at 0° = 0·88. It is insoluble in water, but dissolves in alcohol and in ether, and, although neutral to litmus, dissolves readily in concentrated hydrochloric acid, and slightly in the dilute acid. The aurochloride is oily and insoluble. When heated with hydrochloric acid in sealed tubes at 150°, the cyanamide yields carbonic anhydride, ammonium chloride, and dipropylamine hydrochloride.

Dipropylcarbodiimide, NPr:C:NPr, is obtained by gradually adding dry yellow mercuric oxide to a solution of symmetrical dipropylthiocarbamide in dry benzene until the liquid no longer gives a black precipitate with ammoniacal silver nitrate. It is a mobile liquid, with an odour and taste recalling that of its isomeride, dipropylcyanamide; sp. gr. at 0° = 0·86. It boils at 80° under a pressure of 28 mm. and at 171° under 765 mm., is insoluble in water, but dissolves in alcohol and in ether, and is easily decomposed by acids, even at the ordinary temperature, the products being symmetrical dipropylthiocarbamide if the acid is dilute, but if the acid is concentrated, hydrolysis proceeds further, and carbonic anhydride is given off. C. H. B.

Muscarine. By G. Nothnagel (*Ber.*, **26**, 801—806).—Certain compounds of a natural *muscarine*, from the *Fly agaric*; of artificial *muscarine*, obtained from choline by oxidation with nitric acid (Schmiedeberg and Harnack, *Chem. Centr.*, 1876, 558); and of *anhydromuscarine* (Berlinerblau, Abstr., 1885, 1056; compare E. Fischer, this vol., i, 301), have been prepared, to ascertain how far they differ from each other; *isomuscarine* has been previously studied (Schmidt, Abstr., 1892, 905; Bode, *ibid.*, 806). Anhydromuscarine differs from the others in composition, crystalline form of its platinochloride and aurochloride, and in physiological action. Artificial muscarine and natural muscarine, on the other hand, are alike in crystalline form, in solubility, and composition of their platino- and auro-chlorides, and, to a large extent, in their physiological action. They differ, however, in that artificial muscarine induces paralysis of the intermuscular nerve-terminations in the frog, and myosis in the

pupil of the eyes of birds, whilst natural muscarine does neither of these things; the two substances are, perhaps, physically isomeric.

Acetyltrimethylammonium platinochloride,

$$[NMe_3Cl\cdot CH_2\cdot CH(OEt)_2]_2PtCl_4,$$

forms long prisms, sometimes containing $1H_2O$; the *aurochloride* was also prepared. The base is converted by baryta-water into *anhydromuscarine*, the *platinochloride* of which, $(NMe_3Cl\cdot CH_2\cdot CHO)_2PtCl_4$, forms orange-red, quadratic tables, the *aurochloride* yellow needles. Anhydromuscarine yields, with phenylhydrazine, an unstable hydrazide.

Artificial *muscarine platinochloride*, $[NMe_3Cl\cdot CH_2\cdot CH(OH)_2]_2PtCl_4 + 2H_2O$, crystallises in octahedra, the *aurochloride* in yellow needles. Unlike choline, the base yields neither acetyl nor benzoyl derivatives; when treated either with acetic anhydride or with benzoic chloride, it yields a substance whose platinochloride, $(NMe_3Cl\cdot CH_2\cdot CHO)_2PtCl_4$, melts at 228—229°, and crystallises in octahedra, and is quite different from that of anhydromuscarine. Besides artificial muscarine, *choline nitrite* is formed by the action of nitric acid on choline; its *platinochloride*, $(NMe_3Cl\cdot CH_2\cdot CH_2\cdot O\cdot NO)_2PtCl_4$, melts at 223—224°, and the *aurochloride*, which forms yellow needles, at 240°; the base gives Liebermann's nitroso-reaction.

Natural muscarine yields a *platinochloride*,

$$[NMe_3Cl\cdot CH_2\cdot CH(OH)_2]_2PtCl_4 + 2H_2O,$$

and an *aurochloride* identical in appearance with those of artificial muscarine. A third platinochloride, of similar appearance and composition, was obtained from a base formed by the prolonged action of sodium amalgam on an aqueous solution of betaïne hydrochloride.

C. F. B.

Additive Products and Compounds of Hexamethyleneamine. By H. Moschatos and B. Tollens (*Annalen*, **272**, 271—288; compare Abstr., 1891, 663).—*Hexamethyleneamine phosphate*,

$$C_6H_{12}N_4,H_3PO_4,$$

and the *tartrate*, $C_6H_{12}N_4,C_4H_6O_6$, are crystalline compounds, but the *citrate* is an oil; on adding copper sulphate to a concentrated aqueous solution of hexamethyleneamine, a greenish substance, of the composition $8CuO,2SO_3 + 7H_2O$, is precipitated, whereas with lead nitrate, a basic salt, of the composition $Pb(NO_3)\cdot OH$, is formed.

Hexamethyleneamine combines with phenols in concentrated aqueous solution, yielding crystalline compounds which have, as a rule, no definite melting point; the following compounds were prepared:—*Hexamethyleneamine triphenol*, $C_6H_{12}N_4,3PhOH$; *hexamethyleneamine dicatechol*, $C_6H_{12}N_4,2C_6H_4(OH)_2$; *hexamethyleneamine resorcinol*, $C_6H_{12}N_4,C_6H_4(OH)_2$; *hexamethyleneamine quinol*,

$$C_6H_{12}N_4,C_6H_4(OH)_2;$$

hexamethyleneamine dipyrogallol, $C_6H_{12}N_4,2C_6H_3(OH)_3$; *hexamethylene-*

amine phloroglucinol, $C_6H_{12}N_4,C_6H_3(OH)_3$; *hexamethyleneamine eugenol*, $C_6H_{12}N_4,C_{10}H_{12}O_2$, and the picrate.

The molecular weight of hexamethyleneamine, determined by the cryoscopic method in glacial acetic acid solution, was found to be 121—127°, a result which agrees more closely with that required by the molecular formula $C_6H_{12}N_4$ than the previous determinations of Mayer and Tollens. F. S. K.

Isomerism of Asymmetrical Hydrazones. By A. Claus (*J. pr. Chem.* [2], **47**, 267—273).—This is a discussion of Overton's paper on "Stereochemical Phenylhydrazones" (this vol., i, 208). Claus, as he has already frequently stated, cannot admit that any stereochemical theory is necessary. A. G. B.

Hydrazine Derivatives. By T. Curtius (*Ber.*, **26**, 403—410).—A preliminary account of a series of researches, which are to be described in full at a later date.

Primary acid hydrazines, $R{\cdot}CO{\cdot}NH{\cdot}NH_2$, are obtained by the action of hydrazine hydrate on the acid amide, chloride, or ethereal salt, best from the last-named. Derivatives were prepared from benzoic acid, nitro-, amido-, and hydroxy-benzoic acids, glycollic acid (this hydrazine was formerly described as hydrazineacetic acid, $N_2H_3{\cdot}CH_2{\cdot}COOH$), acetic, formic, hippuric, aceturic, $CMeO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, phthaluric, succinuric, and anilidoacetic acids. Also primary dihydrazines, $R''(CO{\cdot}NH{\cdot}NH_2)_2$, from succinic, malonic, oxalic, and fumaric acids. These primary hydrazines are colourless, solid, non-volatile substances; they crystallise well, and dissolve in water and alcohol, but not in ether. They form hydrochlorides, and the H of the NH group is replaceable by sodium or acetyl. They act as reducing agents, and with aldehydes and ketones condense to tertiary hydrazines.

Secondary acid hydrazines, $R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R$, are obtained by heating the primary hydrazines; hydrazine is not evolved in the reaction to any extent, but is resolved into nitrogen and ammonia. The secondary hydrazines are very stable, insoluble, colourless substances; they melt at a high temperature, and react like acids. To this class must be reckoned phthalylhydrazine, $C_6H_4(CO)_2N_2H_2$, and

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

the product of the action of hydrazine hydrate on carbamide. Secondary dihydrazines, $R''<\begin{matrix}CO{\cdot}NH{\cdot}NH{\cdot}CO\\CO{\cdot}NH{\cdot}NH{\cdot}CO\end{matrix}>R''$, are obtained by the action of nitrous acid on primary dihydrazines.

Acid hydrazoides, $R{\cdot}CO{\cdot}N_3$, are obtained by the action of nitrous acid on the primary hydrazines of monobasic acids. When reduced, some yield acid hydrazines, for example, benzoylhydrazoide yields dibenzoylhydrazine, and, in an analogous manner, diazobenzenimide yields hydrazo- together with azo-benzene. When boiled for some time with water, benzoylhydrazoide loses nitrogen and carbonic acid, and a diamidobenzophenone is formed.

Certain other hydrazines, notably those of hippuric, aceturic, and fumaric acids, react differently with nitrous acid, and form compounds of the type $R{\cdot}CO{\cdot}NH{\cdot}N_2{\cdot}OH$, or $R''(CO{\cdot}NH{\cdot}N_2{\cdot}OH)_2$. When these

compounds are boiled with alcohol, nitrogen and water are lost, and compounds of the type R·CO·NH·OEt are formed.

The action of hydrazine hydrate on ethyl acetoacetate and benzoylacetate, and also on ethyl acetosuccinate and diacetosuccinate, has been studied; the resulting compounds appear to be derivatives of isopyrazolone. Pyrazoline itself, $C_3H_6N_2$, was obtained by the action of hydrazine hydrate on acraldehyde; it is a volatile, readily oxidisable base, dissolves in water, and forms a well crystallised hydrochloride. By the action of hydrazine hydrate on the ethereal salts of γ-keto-acids, such as levulinic, β-benzoylpropionic, and β-benzoylisosuccinic acids, pyridazolone derivatives were finally obtained, hydrazine derivatives being usually formed as intermediate products. Benzoïn yields first a hydrazine, OH·CHPh·CPh:N·NH$_2$, and this, when boiled with alcohol, loses ammonia and forms a ketazine, CPhO·CPh:N·N:CPh·CPhO, which, with hydrazine hydrate, yields 2 mols. of diphenyltrihydrazimethylene, N_2H_2:CPh·CPh:N_2H_2.

Many inorganic double salts of hydrazine have been prepared, and found to resemble the corresponding ammonium salts. Salts of the type $(N_2H_4)_2H_2SO_4$,R″SO$_4$ were prepared in the case of R″ = Cu, Ni, Co, Fe, Mn, Zn, Cd; they are sparingly soluble. With NH$_4$, K, Na, Al, Mg, no such double sulphates were formed. Double chlorides of the type N_2H_4,HCl,RCl were obtained in the case of Hg, Cd, Zn, Fe, and Sn; they are easily soluble, and some of them contain water of crystallisation. Magnesium hydrazine phosphate, analogous to the ammonium phosphate, has also been prepared. In general, hydrazine is thus seen to behave like a mon-acid base. The stable nitrate is N_2H_4,HNO$_3$; the other nitrate, N_2H_4,2HNO$_3$, readily loses half its nitric acid. Free hydrazine is still unknown. C. F. B.

Amidacetaldehyde. By E. Fischer (*Ber.*, **26**, 464—471; compare this vol., i, 187).—*Benzoylamidacetal*, NHBz·CH$_2$·CH(OEt)$_2$, boils under a pressure of 15 mm. at 205—206° (corr.), and decomposes when distilled at the ordinary pressure. Concentrated hydrochloric acid converts it into *hippuraldehyde*, NHBz·CH$_2$·COH, which could not be isolated in the crystalline condition; the *hydrochloride* melts at 110—115°, and is converted into hippuric acid by means of bromine; the *phenylhydrazone* melts at 107—108° (uncorr.).

Benzalamidacetal, CHPh:N·CH$_2$·CH(OEt)$_2$, obtained from benzaldehyde and amidacetal, is a colourless, highly refractive oil, boiling at 156° (corr.) under a pressure of 12 mm. When heated with dilute sulphuric acid, it yields *benzylamidacetal*,

$$CH_2Ph·NH·CH_2·CH(OEt)_2;$$

this boils at 157° (corr.) under a pressure of 16 mm., and at the ordinary pressure between 280° and 290° with partial decomposition. It reduces Fehling's solution after boiling with an acid.

When amidacetal is treated with a mixture of methyl alcohol and methylic iodide, acetaltrimethylammonium iodide is obtained. The corresponding *chloride*, NMe$_3$Cl·CH$_2$·CH(OEt)$_2$, which crystallises in needles, is prepared by shaking a solution of the iodide with silver chloride; concentrated hydrochloric acid converts it into the aldehyde,

$NMe_3Cl\cdot CH_2\cdot COH$. The *platinochloride* forms red, monoclinic crystals, $a : b : c = 0{\cdot}7488 : 1 : 0{\cdot}9906$; $\beta = 76°\ 3'\ 39''$. The aldehyde base corresponding with this may, perhaps, be identical with muscarine.

A. R. L.

Molecular Weight of Metaldehyde. By F. Zecchini (*Gazzetta*, **22**, ii, 586—592).—Hanriot and Oeconomides (Abstr., 1882, 31), from determinations of the vapour density of metaldehyde, concluded that it should be represented as $(C_2H_4O)_3$; these observers also stated that metaldehyde is almost wholly decomposed by boiling chloroform. This, however, the author finds does not hold for dilute solutions; the molecular formula, deduced from boiling point determinations of the most concentrated chloroform solutions (1·3—1·8 per cent.), which can be heated without the occurrence of sensible decomposition, is $(C_2H_4O)_8$. Boiling point determinations of alcoholic solutions lead to molecular weights varying from 6 to 11 times that of aldehyde. Cryoscopic determinations of the molecular weight of metaldehyde dissolved in phenol agree fairly well with the formula $(C_2H_4O)_4$, but are more in accordance with a molecular weight between three and four times that of aldehyde.

W. J. P.

Derivatives of Chloral. By A. Béhal and E. Choay (*Ann. Chim. Phys.* [6], **27**, 319—339; compare Abstr., 1890, 230 and 1093).—Chloral-ammonia very slowly decomposes at the ordinary temperature, the crystals being first converted into a liquid, which after some time separates into two layers, and deposits a crystalline substance. The upper stratum of liquid consists of an aqueous solution of ammonia and ammonium chloride; the lower one yields chloroform and chloraldiformamide on distillation from a water-bath; the crystalline deposit consists of chloraldiformamide and a little ammonium chloride.

Chloraldiformamide, $C_4Cl_3H_5N_2O_2$, melting at 216—217°, has been previously described (*loc. cit.*); when heated with concentrated hydrochloric acid, it is decomposed into chloral, ammonia, and formic acid; as, moreover, the compound can be synthesised by warming anhydrous chloral with formamide, its constitution may be expressed by the formula $CCl_3\cdot CH(NH\cdot CHO)_2$, so that it is not a closed-chain compound, as previously supposed.

Chloralantipyrine, $C_{13}H_{15}Cl_3N_2O_3$, is formed when chloral hydrate is treated with phenylpyrazolone in aqueous solution; it is a crystalline substance, melts at 67—68°, and is moderately easily soluble in water (7·85 parts in 100 at 14°). Its aqueous solution gives a blood-red coloration with ferric chloride, reduces Fehling's solution on warming, and yields chloroform when boiled with potash; when the crystalline substance is heated at a temperature just above 100°, it is converted into a compound of the composition $C_{13}H_{13}Cl_3N_2O_2$, which forms small crystals melting at 186—187°, and insoluble in water. The *acetyl* derivative, $C_{15}H_{15}Cl_3N_2O_3$, prepared by heating chloralantipyrine with acetic anhydride and a trace of zinc chloride, separates from alcohol in crystals melting at 154—155°.

Dichloralantipyrine, $C_{11}H_{12}N_2O,2C_2H_3Cl_3O_2$, prepared in like manner, employing excess of chloral hydrate, melts at 67—68°, and its aqueous

solution gives a blood-red coloration with ferric chloride; 100 parts of water at 14° dissolve 9·98 parts of the substance.

The two compounds described above have a physiological action similar to that of chloral; although they contain such different quantities of the last-named substance, they have, weight for weight, equal toxic properties. F. S. K.

Condensation of Chloral and Butylchloral with Acetone and Acetophenone. By W. Koenigs and E. Wagstaffe (*Ber.*, **26**, 554—559).—Koenigs has already shown (Abstr., 1892, 694) that chloral unites with acetone and acetophenone to form aldol-like condensation products. The present paper gives the results of the further investigation of these substances, and of the compounds obtained in a similar manner from butylchloral.

Chloralacetone, $CCl_3·CH(OH)·CH_2Ac$, crystallises from light petroleum in rhombic pyramids, and forms an *oxime* which melts indefinitely between 95° and 105°. When chloralacetone is boiled for 10 minutes with a 4 per cent. solution of sodium carbonate, it is converted into *β*-acetylacrylic acid, CHAc:CH·COOH, which melts at 125—126°, and has all the properties assigned to it by Wolff (Abstr., 1891, 1185). Owing to the ease with which it is decomposed by alkalis, the yield is not good, and is reduced to a minimum if 1 per cent. potash be employed instead of sodium carbonate.

Chloralacetophenone, $CCl_3·CH(OH)·CH_2·COPh$, separates from light petroleum in compact, monosymmetric crystals; unlike chloral or acetophenone, it has no hypnotic action. Its *oxime*, $C_{16}H_{16}NCl_3O_2$, crystallises from dilute alcohol in white scales melting at 135—137°, and the *hydrazone*, $C_{16}H_{15}N_2Cl_3O$, in yellowish crystals melting at 156—158°. With bromine, it yields a mixture of two *monobromo*-derivatives, which may be separated by fractional crystallisation from light petroleum, the more soluble derivative melting at 105°, and the less soluble at 152—153°. When carefully treated with boiling 1 per cent. potash, it is converted into *phenyl-γ-keto-α-hydroxybutyric acid*, COOH·CH(OH)·CH_2·COPh, which crystallises in white needles melting at 125—126°; the yield is small, as the alkali partially resolves it into acetophenone and oxalic acid The *silver* salt is a white precipitate which may be recrystallised from hot water. When treated with pure sulphuric acid at 0°, the acid loses the elements of water, and is converted into *β*-benzoylacrylic acid, CHBz:CH·COOH, which crystallises from light petroleum in lustrous, yellow needles, and is identical with the benzoylacrylic acid obtained by Pechmann from maleïc anhydride and benzene in presence of aluminium chloride (Abstr., 1882, 1075). The phenylketo-*α*-hydroxybutyric acid recently prepared by Fischer and Stewart (Abstr., 1892, 1448) is not identical with that obtained by the authors, and has, therefore, probably the constitution $CH_2Ph·CO·CH(OH)·COOH$.

Butylchloral and acetophenone unite together when heated with an excess of acetic acid for 15—20 hours, and the resulting *butylchloralacetophenone*, CHMeCl·CCl_2·CH(OH)·CH_2·COPh, which crystallises in white prisms, melts at 108—110°, and volatilises in a current of steam. When treated with pure sulphuric acid in the cold, it is converted

into *trichlorobutylideneacetophenone*, $CHMeCl\cdot CCl_2\cdot CH{:}CH\cdot COPh$, which crystallises from light petroleum in white plates, melts at 45—47°, and is also volatile in steam. H. G. C.

Chlorination of Acetone. By P. Fritsch (*Ber.*, **26**, 597—598).—The author finds that monochloracetone, prepared by Barbaglia's process, is a somewhat complex mixture, a conclusion in agreement with that of Tcherniac (Abstr., 1892, 1425). Even when chlorine is passed into acetone in quantity sufficient to convert only one-half of the ketone into its monochloro-derivative, the fraction of the product boiling at 119—120° is impure, doubtless owing to the presence of mesityl oxide.

For the preparation of pure monochloracetone, the following method is recommended:—The acetone is mixed with about one-third of its weight of marble, and, during chlorination, water is slowly dropped into the cooled liquid in order to dissolve the calcium chloride; the process is interrupted before the whole of the marble is dissolved, and the mixture is kept at a moderate temperature until the evolution of carbonic anhydride is at an end; pure monochloracetone boiling at 118—120° can then be isolated from the product by fractional distillation. When molecular proportions of acetone and marble are used, and chlorine is passed until the latter is almost completely dissolved, about 90 per cent. of a mixture of mono- and di-chloracetone boiling at 118—120°, and about 10 per cent. of symmetrical dichloracetone melting at 44°, are obtained.

When monochloracetone is treated with chlorine at 100° in sunlight as long as the gas is absorbed, the principal product is pentachloracetone boiling at about 190—195°. F. S. K.

Action of Nitric acid on Acetone. By R. Behrend and J. Schmitz (*Ber.*, **26**, 626—628).—A yellow, very unstable oil which seems to consist for the most part of *hydroxyisonitrosoacetone nitrite*, $COMe\cdot C(NOH)\cdot O\cdot NO$, is formed, together with carbonic oxide, carbonic anhydride, nitrous oxide, nitrogen, ammonia, acetic acid, and oxalic acid, when acetone is carefully treated with nitric acid of sp. gr. 1·37, to which a little red fuming acid has been added. It is decomposed by concentrated hydrochloric acid, with evolution of gas, yielding *chlorisonitrosoacetone*, $COMe\cdot CCl{:}NOH$; this compound melts at 104·5—105·5°, and combines with hydroxylamine to form chloromethylglyoxime, which decomposes at about 175°; chlorisonitrosoacetone is decomposed by boiling dilute sulphuric acid, the products being acetic, formic, and hydrochloric acids and hydroxylamine.

The *oxime*, $C_3H_5N_3O_4$, is obtained when an aqueous solution of the yellow, unstable oil is treated with hydroxylamine hydrochloride. When the crude crystalline product is dissolved in ether, and the solution is mixed with light petroleum, a small quantity of an oxime, which decomposes at about 148°, is precipitated; on evaporating the solution large, transparent crystals, which contain ether and effloresce on exposure to the air, are deposited; these crystals, when free from ether, decompose at 97—98°, but sinter at about 80°. The oxime gives Liebermann's reaction, is very unstable, and decomposes with

evolution of ruddy fumes, even when kept in closed vessels or when warmed with benzene or chloroform; on treatment with concentrated hydrochloric acid, it yields chlorisonitrosoacetone and a small quantity of chloromethylglyoxime, with evolution of gas. On adding sodium carbonate to an aqueous solution of the oxime, carbonic anhydride is liberated, the solution turns yellow, and a sparingly soluble, crystalline powder is precipitated, sodium nitrite remaining in solution; the crystalline precipitate separates from hot alcohol in small needles, decomposes at about 191°, dissolves in alkalis yielding colourless solutions, and has the composition $C_3H_4N_2O_2$.

The *hydrazone*, $N_2HPh{:}CMe{\cdot}C(NOH){\cdot}O{\cdot}NO$, is produced, together with a small quantity of a hydrazone which decomposes at about 177°, when the yellow, unstable oil is treated with phenylhydrazine hydrochloride; it crystallises from a mixture of ether and petroleum in long, transparent, amber-yellow prisms or plates, which contain ether, effloresce on exposure to the air, and decompose at 125°.

F. S. K.

Formation of Phoronic acid from Phorone. By R. Anschütz (*Ber.*, **26**, 827—828).—Phorone, melting at 28°, prepared from acetone and hydrochloric acid, is treated with gaseous hydrogen chloride until it has taken up 2 molecular proportions of the latter, the product is boiled in alcoholic solution with potassium cyanide, and the phorononitrile which separates on warming with fuming hydrochloric acid is hydrolysed, and yields phoronic acid melting at 184°; hence the formulæ previously assigned to phorone, $CMe_2{:}CH{\cdot}CO{\cdot}CH{\cdot}CMe_2$, and to phoronic acid,

$$COOH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}COOH,$$

are confirmed.

C. F. B.

New Mercurammonium Salts. By E. Balestra (*Gazzetta*, **22**, ii, 563—569).—*Mercurammonium acetate*, $NHg_2{\cdot}OAc$, is obtained as a white powder on digesting yellow mercuric oxide with ammonium acetate solution; it becomes slightly yellow on exposure to air, and is turned brown by light. It dissolves in hydrochloric acid or ammonium acetate, but is insoluble in water.

Mercurammonium ammonium acetate, $NHg_2{\cdot}AcO,3NH_4{\cdot}OAc,H_2O$, is obtained in deliquescent, colourless prisms by the slow evaporation of mercuric acetate solution rendered slightly alkaline by ammonia; the same salt is formed on saturating a concentrated solution of ammonium acetate with yellow mercuric oxide. It is soluble in a little water without decomposition, but mercurammonium acetate separates on adding much water.

Mercurammonium tartrate, $(NHg_2)_2C_4H_4O_6.2\frac{1}{2}H_2O$, is prepared by spontaneous evaporation of a solution of mercuric tartrate in ammonia or of yellow mercuric oxide in ammoniacal ammonium tartrate solution. It forms colourless, prismatic masses, is very sensitive to light, and is soluble in hydrochloric acid, potassium iodide, sodium thiosulphate, and ammonium acetate or tartrate solutions, but insoluble in water.

Mercurammonium ammonium tartrate,

$$2(NHg_2)_2C_4H_4O_6,(NH_4)_2C_4H_4O_6,H_2O,$$

separates as a white, amorphous powder when yellow mercuric oxide is dissolved in ammonium tartrate; it resembles the preceding salt in chemical properties.

Mercurammonium ammonium salicylate,

$$2NHg_2{\cdot}C_7H_5O_3{,}5NH_4{\cdot}C_7H_5O_3,$$

separates in opaque prisms from a solution of yellow mercuric oxide in ammonium salicylate. It dissolves in ammonium acetate, tartrate, or bromide, hydrochloric acid, or potassium iodide solutions, but is decomposed by water. W. J. P.

Mixed Anhydrides of Hypochlorous and analogous acids. By T. Selivanoff (*Ber.*, **26**, 423—426; compare this vol., i, 192).—Bromylacetamide, NHAcBr ("acetobromamide" of Hofmann), is shown to be a substituted amide of hypobromous acid, for when it is distilled with water at a low pressure the distillate contains much hypobromous acid and but little bromine, and acetamide is regenerated. Moreover, from a solution of potassium iodide acidified with acetic acid, 1 mol. of bromylacetamide liberates 2 atoms of iodine, and thus reacts like 1 mol. of hypobromous acid. Dibromylacetamide, $NAcBr_2$, in a similar way displaces 4 atoms of iodine, and is thus to be regarded as a substituted imide of hypobromous acid (2 mols.). With amines and acid amides, bromylacetamide behaves like the analogous chlorine compound. With dipropylamine, it yields acetamide and *bromyldipropylamide*, NPr_2Br, the latter as an oil. With succinimide, it yields *bromylsuccinimide*, $C_2H_4{\cdot}C_2O_2{\cdot}NBr$, melting at 161—162°; this substance can also be synthesised from succinimide and hypobromous acid, or bromine and an alkali, and it is decomposed by water into hypobromous acid and succinimide. With ethylic imidocarbonate, it yields the *bromylimidocarbonate*, $NBr{:}C(OEt)_2$, 1 mol. of which also liberates 2 atoms of iodine. With amylamine, it yields *dibromylamylamide*, $NAmBr_2$, as a reddish-brown, unstable oil, with a strong, unpleasant odour; in the presence of water it reacts like 2 mols. of hypobromous acid. Besides the above-mentioned compounds, *bromyldimethylamide*, NMe_2Br, *dibromylethylamide*, $NEtBr_2$, and *bromyldiisobutylamide*, NBu^{β}_2Br, were prepared. These substances react like those already described; they are less stable than the corresponding chlorine compounds, and are more easily hydrolysed. Some of the secondary amine derivatives are explosive.

C. F. B.

Synthesis with the aid of Ethylic Cyanacetate and Ethylic Cyanosuccinate. By L. Barthe (*Ann. Chim. Phys.* [6], **27**, 239—288).—The experiments which have been previously recorded in various short papers (Abstr., 1889, 588, 708; 1891, 42, 43, 1017) are now communicated in a systematic form, but without any new facts of importance being given. F. S. K.

Oxidation Products of Behenolic acid. By O. v. Grossmann (*Ber.*, **26**, 639—649).—Behenolic acid is prepared by the bromination of erucic acid and treatment of the product with potash at 180°; the yield is about 75 per cent. of the theoretical.

On oxidising behenolic acid with concentrated fuming (red) nitric

acid, carbonic anhydride is evolved; the oily portion is separated, and steam distilled, when the distillate consists of pelargonic acid and ethyl pelargonate, together with a small quantity of an acid which gives a yellow, crystalline barium salt, and is probably nitroso-pelargonic acid. The non-volatile residue contains dioxybehenolic acid (m. p. 93·5°), and arachic acid (m. p. 73·5°), which are separated by means of light petroleum, in which the former is insoluble.

The aqueous nitric acid solution contains brassylic acid, which, contrary to the statements of Haussknecht, melts at 112°, has the formula $C_{13}H_{24}O_2$, and is formed, together with pelargonic acid, by the action of fuming nitric acid on dioxybehenolic acid. The *barium salt* crystallises with 2 mols. H_2O; the *calcium* and *copper salts* with 1 mol. H_2O; whilst the *silver salt* is anhydrous.

Behenolic acid, on fusion with potash, yields arachic acid and acetic acid.

Two distinct reactions appear to take place during the oxidation of behenolic acid, $CH_2Me\cdot[CH_2]_{17}\cdot C{:}C\cdot COOH$; on the one hand, it yields carbonic anhydride and arachic acid, $CH_2Me\cdot[CH_2]_{17}\cdot COOH$, whilst a portion of it is converted into dioxybehenolic acid,

$$CH_2Me\cdot[CH_2]_6\cdot CO\cdot CO\cdot[CH_2]_{11}\cdot COOH,$$

which is then resolved into pelargonic acid, $CH_2Me\cdot[CH_2]_6\cdot COOH$, and brassylic acid, $COOH\cdot[CH_2]_{11}\cdot COOH$. The author does not consider that "behenolic acid" is an isomeric mixture, but that the nitric acid causes an intramolecular rearrangement of the hydrogen atoms. J. B. T.

Heintz's Glycollide. By R. Anschütz (*Ber.*, **26**, 560—562; compare this vol., i, 165, and Bischoff and Walden, this vol., i, 250).—The author shows, by reference to Heintz's paper (*Pogg. Ann.*, **109**, 484), that the latter had in his hands the diglycollide corresponding to lactide, having obtained it as a crystalline substance by distilling glycollic acid in a current of carbonic anhydride. He appears not to have further investigated this substance after finding that glycollic acid, on heating at 240°, gives the glycollide melting at 220°, which he supposed to correspond with lactide. The author has repeated Heintz's experiment, carrying out the distillation under diminished pressure, and finds that the substance thus obtained has the composition $C_2H_2O_2$, and like dilactide, but unlike the glycollide already known, is soluble in chloroform, after crystallising from which it melts at 82—83°. When again distilled under diminished pressure, it passes into polyglycollide. H. G. C.

Ethylic Carbacetoacetate. By P. Genvresse (*Bull. Soc. Chim.* [3], **7**, 586—587).—A rejoinder to Hantzsch (Abstr., 1892, 819).—The author states that he has experimentally proved the non-identity of the so-called ethylic carbacetoacetate and ethylic isodehydracetate. In repeating Hantzsch's experiments, he has not obtained the homomesaconic acid described by the latter, but two entirely different acids, in accordance with Anschütz's results (Abstr., 1892, 172). A. R. L.

Action of Iodic acid on Malonic acid. By A. Angeli (*Ber.*, **26**, 595—597).—*Triiodacetic acid*, $CI_3 \cdot COOH$, is obtained when malonic acid is treated with a hot aqueous solution of iodic acid, and the mixture boiled until a rapid evolution of carbonic anhydride commences; if, after cooling quickly, the solution be kept for 2 or 3 days, the new acid is deposited in lustrous, yellow crystals, which turn brown at 100°, and melt at 150° with decomposition; it is decomposed by warm acetic acid into iodoform and carbonic anhydride.

Diiodacetic acid is also formed when malonic acid is treated with iodic acid, and can be obtained as the principal product by boiling the solution until the evolution of carbonic anhydride is at an end, filtering from the precipitated triiodo-derivative, and again boiling for some time; on cooling, the acid is deposited in pale yellow needles melting at 110°. F. S. K.

Ethereal Salts of Pyrotartaric acid. By R. Braunschweig (*J. pr. Chem.* [2], **47**, 274—300).—The etherification of pyrotartaric acid with methyl or ethyl alcohol gives rise to mixtures of normal and acid ethereal salts, in which the former predominate. It is not settled whether the acid salts belong to the ortho-series,

$$COOR \cdot CH_2 \cdot CHMe \cdot COOH,$$

or the allo-series, $COOH \cdot CH_2 \cdot CHMe \cdot COOR$, or to both; they are also obtainable by heating pyrotartaric anhydride with the corresponding alcohol, as in the case of the ortho-salts of camphoric acid. By treating an alcoholic solution of pyrotartaric anhydride with sodium or sodium alkyloxide, the sodium ethereal salt is obtained, and the acid ethereal salt obtained by decomposing this is found to be identical with that obtained directly, as indicated above. The acid salts can also be prepared by partial hydrolysis of the normal salts, but whether the products belong to the allo- or ortho-series is not settled. The mixed salts are difficult to obtain, and isomerides have not yet been isolated.

Dimethylic pyrotartrate may be prepared by saturating a solution of pyrotartaric acid in methyl alcohol with dry hydrogen chloride, precipitating the oily product by a solution of salt, dissolving it in light petroleum, and extracting any methylic hydrogen pyrotartrate from this solution by a weak alkali. It is a colourless liquid, has a peculiar odour, boils at 197° (759 mm.), and dissolves in water, from which it is separated by salt. Its optical properties are detailed.

Orthomethylic pyrotartrate is prepared by heating pyrotartaric anhydride (b. p. 240—240·5°, obtained by heating pyrotartaric acid in a stream of air as long as water is expelled) with methyl alcohol in a reflux apparatus. It is a colourless, strongly acid liquid, which boils at 153—153·5° (20 mm.); it dissolves in water, but may be salted out again unless it has been left long enough to undergo hydrolysis into methyl alcohol and pyrotartaric acid. The *sodium derivative* is obtained as a gelatinous precipitate by adding sodium methoxide to a solution of pyrotartaric anhydride in glacial acetic acid.

Orthoethylic pyrotartrate is similarly prepared; it is a colourless, odourless oil, boils at 160—161° (22 mm.), and dissolves in water, from which it may be salted out. The *sodium derivative* was prepared.

Experiments made with the object of obtaining mixed alkyl pyrotartrates are detailed. The *ethylic methylic* salt, prepared by the action of sodium on a mixture of the orthoethylic salt and methylic iodide, was found to be a colourless, refractive liquid, which distilled for the most part at 198—199° (754·1 mm.); its optical properties are given.

A. G. B.

Trichloropyruvic acid. By O. Büchner (*Ber.*, **26**, 656—658).—Chlorofumaric acid is dissolved in 6 parts of water, and the solution repeatedly saturated with chlorine until the colour is permanent; the operation requires about two weeks; after extraction with ether and crystallisation from chloroform, trichloropyruvic acid,

$$CCl_3{\cdot}C(OH)_2{\cdot}COOH,$$

is obtained, and is identical with "isotrichloroglyceric acid" prepared by Schreder from gallic acid and salicylic acid by the action of hydrochloric acid and potassium chlorate, and by Claisen and Antweiler from trichloracetyl cyanide. On treatment with alkalis, hydroxylamine, or phenylhydrazine at the ordinary temperature, it is resolved into oxalic acid and chloroform; by reduction in acid solution, hydroxypropionic acid is formed. *Ethylic trichloropyruvate* boils at 110° under a pressure of 21 mm.; it forms colourless crystals containing 1 mol. H_2O, and melts at 34·5°.

J. B. T.

Action of Hydrogen Sulphide on Pyruvic acid. By J. M. Lovén (*J. pr. Chem.* [2], **47**, 173—182).—The author has already dealt with this subject (Abstr., 1884, 1298); he further discusses the trithiodilactylic acid, $C_6H_{10}S_3O_4$, obtained by saturating a 50 per cent. aqueous solution of pyruvic acid with hydrogen sulphide, and adding fuming hydrochloric acid until the solution becomes turbid. The oily liquid which now separates soon crystallises, and may be recrystallised from chloroform. It forms lustrous laminæ, melts at 95°, and dissolves in hot water, from which it separates out on cooling in the oily form, but afterwards solidifies; dilute acids dissolve it but little. It has an acid reaction, and decomposes carbonates. Alkalis remove sulphur from it, even in the cold. Lead acetate gives a white and copper acetate a greenish precipitate, with the acid, but both precipitates soon turn black from formation of sulphide. By elimination of sulphur, it yields dithiodilactylic acid (*loc. cit.*); by reduction with hydrogen it yields hydrogen sulphide and thiolactic acid; by oxidation, it yields barium α-sulphopropionate. From these reactions, the author deduces that the formula $S(S{\cdot}C_2H_4{\cdot}COOH)_2$ correctly represents the constitution of the acid.

A. G. B.

Solubility of Cream of Tartar in Dilute Alcohol. By W. H. Wenger (*Amer. Chem. J.*, **14**, 624—625).—The figures in the lower line give the number of grams of cream of tartar which dissolve at 25° in 1000 c.c. of aqueous alcohol of the percentage strength given by the corresponding figure in the upper line.

90.	80	70.	60.	50.	40.	30.	20.	10.	Water.
0·15	0·19	0·30	0·41	0·79	1·32	1·96	3·01	4·51	5·76

C. F. B.

Constitution of Leucine. By E. Schulze and A. Likiernik (*Zeit. physiol. Chem.*, **17**, 513—535).—A full account is given of experiments previously published (Abstr., 1891, 681). In addition, it is found that leucine prepared from various sources, fibrin, elastic tissue, &c., has the same properties as those already described in the leucine obtained from conglutin. W. D. H.

Nucleïn Bases. By C. Wulff (*Zeit. physiol. Chem.*, **17**, 468—510).—The following method is recommended for the separation of guanine from guano. It is boiled for four hours with dilute sulphuric acid, cooled, and filtered; the filtrate is made alkaline with sodium hydroxide and again filtered. To the filtrate, ammoniacal silver solution is added, to precipitate the guanine and uric acid; this precipitate is washed with cold water and hot water, and then treated with hot dilute hydrochloric acid, the silver chloride filtered off, and the filtrate decolorised with animal charcoal; the guanine is then precipitated therefrom by ammonia; a small quantity of urea in hot nitric acid is added, and the mixture is set aside to crystallise. The guanine nitrate, now free from uric acid, is dissolved in dilute sodium hydroxide and the guanine precipitated by ammonium chloride. This last procedure gets rid of traces of xanthine.

Guanine exists in guano partly as a calcium compound and partly in substances like nucleïn. From these it is liberated by the preliminary treatment with hot sulphuric acid.

The decomposition of guanine by hydrochloric acid is represented by the equation $C_5H_5N_5O + 7H_2O = 4NH_3 + C_2H_5NO_2 + 2CO_2 + CH_2O_2$.

The compounds of guanine investigated were the *dichromate*, $C_5H_5N_5O,H_2Cr_2O_7$, orange-coloured, four-sided prisms, giving off water when heated at 100°; the *picrate*, $C_5H_5N_5O,C_6H_3N_3O_7 + H_2O$, yellow needles, losing water of crystallisation at 110° and decomposing at 190°; the *ferricyanide*, $(C_5H_5N_5O)_4,H_3Fe(CN)_6 + 8H_2O$, brown, six-sided prisms, losing water of crystallisation at 120—130°; the *nitroferricyanide*, $(C_5H_5N_5O)_2,H_2(CN)_5NOFe + 1\frac{1}{2}H_2O$, four-sided prisms; the *metaphosphate*, $C_5H_5N_5O,HPO_3 + xH_2O$, readily soluble in water and dilute acids, but sparingly in ammonia; these solubilities go against Liebermann's hypothesis, that nucleïn is proteïd metaphosphate; adenine forms an analogous compound. The *silver picrate*,

$$C_5H_4AgN_5O,C_6H_3N_3O_7 + 1\tfrac{1}{2}H_2O,$$

is sparingly soluble in hot, insoluble in cold water; the *bismuthoiodide* has the formula $C_5H_5N_5O,HI,2BiI_3 + 2H_2O$.

Acetylguanine, $C_5H_4N_5OAc$, is crystalline and sparingly soluble in water, alcohol, and ether, it may be heated to 260° without change; *propionylguanine*, $C_5H_4N_5O{\cdot}COEt$, is crystalline and may be heated to 260° without change; *benzoylguanine*, $C_5H_4N_5O{\cdot}COC_6H_5$, is crystalline, obtainable with difficulty in small quantities; and a crystalline ethylguanine, $C_5H_4EtN_5O$, may be heated to 280° without change. Attempts to obtain a dimethyl derivative failed.

The formation of the picrate is recommended for estimation of

guanine. Full details with test experiments are given. Metaphosphoric acid may be used for the separation of guanine from hypoxanthine and adenine, but there are difficulties yet to be overcome.

An appendix to the paper gives details concerning hypoxanthine picrate, adenine metaphosphate, and adenine aurochloride.

W. D. H.

Oxidation Products of some Substances containing the Group of Atoms $C_2N_2O_2$. By A. Angeli (*Ber.*, **26**, 593—595).—The peroxides of certain fatty oximes containing aromatic radicles, that is to say, compounds of the general formula $\begin{matrix}CMe—CR\\ \| \quad\quad \|\\ N\cdot O\cdot O\cdot N\end{matrix}$, such as those derived from isosafrole, isoapiole, &c., contain a very stable closed chain, and, on treatment with potassium permanganate, are sometimes converted into acids simply by the oxidation of the aromatic radicle.

An *acid* of the constitution $\begin{matrix}N{:}CMe\\ |\\ O\cdot O\cdot N\end{matrix}\!\!>C\cdot COOH$ is formed when diisonitrosoisosafrole peroxide, $\begin{matrix}N{:}CMe\\ |\\ O\cdot O\cdot N\end{matrix}\!\!>C\cdot C_6H_3\!<\!\begin{matrix}O\\ O\end{matrix}\!>CH_2$, is oxidised with potasssium permanganate in alkaline solution; it crystallises in colourless plates or needles, and melts at 92°. That the constitution of this compound is expressed by the formula given above, is shown by the fact that it can also be obtained by oxidising $\alpha\beta$-diisonitrosobutyric acid with ice-cold nitric acid of sp. gr. 1·45.

It would seem that the direct combination of an unsaturated compound with nitrous acid is greatly facilitated when the former contains two double linkings in close proximity, even when one is present in a closed chain; derivatives of propenylbenzene, for example, are readily converted into crystalline compounds of the general formula $R\cdot C_3H_5\cdot N_2O_3$ and $R\cdot C_3H_3\cdot N_2O_2$, whereas the corresponding allyl derivatives are practically unchanged under the same conditions. Again, crotonic acid does not yield an additive product with nitrous acid, whereas sorbic acid, which, according to Fittig, has the constitution $CHMe{:}CH\cdot CH{:}CH\cdot COOH$, is readily converted into a nitrosite.

F. S. K.

Nitrogen Halogen Compounds. By F. Lengfeld and J. Stieglitz (*Amer. Chem. J.*, **15**, 215—222).—*Bromosuccinimide*, $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>NBr$, is obtained by the action of bromine (32 grams) on succinimide (20 grams) dissolved in ice-cold aqueous soda (8 grams to 50 c.c.). It crystallises from hot benzene in colourless, tetragonal prisms, and melts at 172·5° when slowly heated, but at 177·5—178·5° when rapidly heated. With acids, bromine is liberated, and succinimide regenerated, whilst with ammonia, nitrogen is evolved. It is slowly decomposed by water, but is quite stable when dry. When boiled with sodium methoxide (1 mol.) in dilute methyl alcohol solution, it forms two compounds, one of which, *methoxysuccinamic*

acid, $OMe{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, a colourless, crystalline substance melting at 77—77·5°, and formed only in small quantity, is sparingly soluble in ether, and the other, the *methylic salt* of this acid, a colourless, crystalline substance melting at 33·5° and boiling at 145·5—146·5° under 20 mm. pressure, is easily soluble. When the sodium methoxide solution is concentrated, a small quantity of methylic methoxysuccinamate is formed, together with some succinimide, but the greater part of the product consists of a colourless, crystalline substance, $C_{10}H_{16}O_6N_2$, which is hydrolysed by cold, concentrated hydrochloric acid yielding succinic acid and a neutral, colourless, crystalline substance, $C_4H_6O_2N_2$, melting with decomposition at 272°. The latter may also be obtained from the former by boiling it with a methyl alcohol solution of sodium methoxide (1 mol.). JN. W.

Furfuryl Alcohol and its Derivatives. By L. v. WISSELL and B. TOLLENS (*Annalen*, **272**, 291—306).—Furfuryl alcohol, prepared by Schiff's method (Abstr., 1891, 676) and purified by distillation with steam, boils at 168—170°, and is soluble in water; its sp. gr. is 1·1354 at 20°/20°. Like pyrroline, it is very sensitive to mineral acids; the pure alcohol does not redden aniline acetate paper.

Furfuryl methyl ether, $C_5H_3O{\cdot}OMe$, obtained by treating furfuryl alcohol with potassium hydroxide and methylic iodide, is a colourless, pleasant smelling liquid of sp. gr. 1·0315 at 20°/20°, and boils at 134—136°.

Furfuryl ethyl ether, $C_5H_3O{\cdot}OEt$, is a mobile oil of sp. gr. 0·9884 at 20°/20°; it boils at 148—150°. The *propyl ether*, $C_5H_3O{\cdot}OPr$, boils at 164—168°; its sp. gr. is 0·9722 at 20°/20°. The *amyl ether*, $C_5H_3O{\cdot}O{\cdot}C_5H_{11}$, boils at 196—198°, and is specifically lighter than water.

Furfurylic benzoate, $C_5H_3O{\cdot}OBz$, prepared by shaking the alcohol with soda and benzoic chloride, seems to boil at 275—285°; its sp. gr. is about 1·1766 at 20°/20°. The corresponding *acetate*, $C_5H_3O{\cdot}OAc$, boils at 175—177°; its sp. gr. is 1·1175 at 20°/20°. F. S. K.

Methylfurfuraldehyde and Methylpyromucic acid. By H. B. HILL and W. L. JENNINGS (*Amer. Chem. J.*, **15**, 159—185).—Wood was subjected to dry distillation at a comparatively low temperature, and a considerable amount of furfuraldehyde was formed, together with substances of higher boiling point (175—250°), which were ultimately resolved by fractionation with a Hempel bead column into two liquids, boiling at 184—186° and 200—220° respectively. The first, nearly colourless, and forming the larger part of the product, showed the general properties of an aldehyde, and on purification by means of the hydrogen sodium sulphite compound, proved to be methylfurfuraldehyde, boiling at 186—187° (corr.) under a pressure of 760 mm., and having a sp. gr. of 1·1087 at 18°/18°. It smells like its lower homologue, forms a liquid hydrazone with phenylhydrazine, gives colour tests with diazobenzenesulphonic acid, with resorcinol and hydrochloric acid (orange-red), and with pyrogallol (carmine), but apparently does not restore the colour to rosaniline decolorised by sulphurous acid. With aqueous ammonia, like aromatic aldehydes, it

yields *methylfurfuramide*, $C_{18}H_{18}N_2O_3$, a substance crystallising in slender, radiating needles, and melting at 86—87°. Both methylfurfuraldehyde and its lower homologue are converted quantitatively into the corresponding acids by oxidation with silver oxide in boiling aqueous solution.

Methylpyromucic acid, $C_4OH_2Me{\cdot}COOH$, crystallises in hexagonal prisms or plates, melts at 108—109°, and sublimes readily at low temperatures. The *barium salt* (anhydrous), *calcium salt*, with $2H_2O$, *silver salt* (anhydrous), *sodium salt* (anhydrous) and *potassium salt* (anhydrous) are described. The *ethylic salt* boils at 213—214° under a pressure of 766 mm., and does not crystallise. It is converted by ammonia into *methylpyromucamide*, $C_4OH_2Me{\cdot}CONH_2$, which forms long, colourless prisms, and melts at 131°. Methylpyromucic acid is oxidised by moist bromine (2 mols.), with elimination of carbonic anhydride, yielding β-acetacrylic acid, $CHAc{:}CH{\cdot}COOH$, melting at 123—124°, but by the addition of bromine, it is converted into $\alpha\beta$-dibromolevulinic acid, melting at 107—108°, which yields a phenylhydrazone, $NHPh{\cdot}N{:}CMe{\cdot}CH{:}CH{\cdot}COOH$, melting at 156—157°. The methyl group of methylpyromucic acid is, therefore, in the δ-position. Methylpyromucic acid is converted by fuming sulphuric acid into a *sulphomethylpyromucic acid*, in which the sulphonic group is probably in the β-position. Dry bromine acting in the cold (in glacial acetic acid solution) effects nuclear substitution, as in aromatic compounds, a *bromomethylpyromucic acid*, $C_4OHBrMe{\cdot}COOH$, being formed, which crystallises in colourless, branching needles and melts at 150—151°. The *barium salt* with $4H_2O$, *calcium salt* with $3H_2O$, *silver salt* (anhydrous), and *potassium salt* (anhydrous) are described. Moist bromine (bromine vapour, 2 mols., passed into aqueous solution) or dilute nitric acid oxidises and hydrolyses the bromo-acid into a bromacetylacrylic acid melting at 61°, the exact constitution of which has not yet been determined. A small quantity of a crystalline substance melting at 90—91° and containing a large amount of bromine is simultaneously formed by the action of the latter. Bromine acting on methylpyromucic acid in boiling carbon bisulphide or chloroform solution effects substitution in the lateral chain, again as with aromatic compounds, *ω-bromomethylpyromucic acid*, $CH_2Br{\cdot}C_4OH_2{\cdot}COOH$, being formed. This crystallises in small, clustered, oblique plates, and melts at 147—148°. It is hydrolysed by hot water into hydrogen bromide and *ω-hydroxymethylpyromucic acid*, $OH{\cdot}CH_2{\cdot}C_4OH_2{\cdot}COOH$, melting at 162—163°, and thus resembles the aromatic lateral chain substitution products. By brominating the nucleal bromomethylpyromucic acid in boiling chloroform, lateral chain substitution is effected, and *$\omega\beta$-dibromomethylpyromucic acid* is formed. This crystallises in small, oblique tables, and melts with decomposition at 175°. It is hydrolysed by water into *ω-hydroxy-β-bromomethylpyromucic acid*, which crystallises in oblique prisms, and melts at 153—154°. The *barium salt* is mentioned. Like aromatic compounds, methylpyromucic acid forms unstable additive products. The acid in chloroform solution, for instance, when cooled by a freezing mixture, takes up bromine (4 atoms) to form the tetrabromide of methylpyromucic acid,

$C_4OH_2MeBr_4$·COOH, which crystallises in flat needles, and melts with decomposition at about 95°.

The fraction boiling at 200—220° was extracted with alkali, and the acidified alkaline extract distilled with steam; an oil was obtained which boiled at 200—205°, and proved to be guaiacol (orthomethoxyphenol), since it was converted by bromine into tribromoguaiacol (m. p. 115—116°) and the latter by hydrolysis into catechol (m. p. 103—104°; b. p. 240—242°). Jn. W.

Derivatives of Pyromucamide. By C. E. Saunders (*Amer. Chem. J.*, **15**, 130—137).—*βδ-Dibromofurfuronitrile* is prepared by dissolving βδ-dibromopyromucamide in bromine (6 atomic proportions) and treating the solution with a cold 5 per cent. solution of sodium hydroxide, when it rises to the surface. It was also obtained by dehydrating βδ-dibromopyromucamide by means of phosphorus pentachloride. It crystallises from superheated alcohol in colourless laminæ, has a characteristic odour, melts at 88° (uncorr.), boils at 225° (uncorr.), and can be sublimed; it dissolves in ether and hot alcohol, but hardly at all in water. When acted on by concentrated hydrochloric acid, it yields the original amide and βδ-dibromopyromucic acid.

Pyromucamide tetrabromide is obtained by the direct action of bromine on pyromucamide below 0°. It forms colourless, lustrous crystals, melts about 121°, and dissolves to some extent in ethylic acetate and acetone, but is almost insoluble in most other organic solvents and quite insoluble in water. It is decomposed by boiling with water, glacial acetic acid, or alcohol. Alkalis decompose it with the formation of βγ-dibromopyromucic acid.

When pyromucamide is dissolved in bromine water and the solution is made alkaline, a dark blue (or purple) colour is produced. If aniline be the base employed, a reddish precipitate is produced, which melts with decomposition at 78°. When phenylhydrazine is used, a brilliant, red precipitate is obtained; this can be crystallised from an alcoholic solution saturated at 50°; its composition is $C_{11}H_{11}N_3O_2$, corresponding with a compound of 1 mol. of phenylhydrazine with 1 mol. of pyromucamide, less 2 atoms of hydrogen. It is being further investigated. A. G. B.

Chlorosulphopyromucic acids. By H. B. Hill and W. S. Hendrixson (*Amer. Chem. J.*, **15**, 145—158).—β-Chloropyromucic acid, prepared by the action of sodium amalgam on the βγ-dichloro-acid, is converted by fuming sulphuric acid into *β-chloro-δ-sulphopyromucic acid*, $SO_3H·C_4OHCl·COOH$, which crystallises in hemispherical masses of indistinct, radiating needles, and is deliquescent. The *barium salt* (+ H_2O), *lead salt* (+ $4H_2O$), and *potassium salt* (+ H_2O) are described. On attempting to eliminate the chlorine by means of sodium amalgam in alkaline solution, the sulphonic group is itself eliminated, and the chloro-acid re-formed. This behaviour is characteristic of the δ-sulphopyromucic acids. The sulphonic group is also eliminated by oxidation with bromine, chlorofumaric acid apparently

being formed. Fuming nitric acid converts the chlorosulphonic acid into the corresponding *β-chloro-δ-nitropyromucic acid* with H_2O.

βγ-Dichloropyromucic acid is converted by fuming sulphuric acid into *βγ-dichloro-δ-sulphopyromucic acid*, $SO_3H{\cdot}C_4OCl_2{\cdot}COOH$, which crystallises in radiating needles and is deliquescent. The *barium salt* with $5H_2O$, *lead salt* with $3H_2O$, and *potassium salt* with H_2O are described. The sulphonic group is eliminated by oxidation with bromine, dichloromaleïc acid being formed.

δ-Chloropyromucic acid is converted by fuming sulphuric acid into *β-sulpho-δ-chloropyromucic acid*, which crystallises in dendritic needles. The *barium salt* with $5H_2O$, *acid barium salt* with $4H_2O$, *calcium salt* with $2H_2O$, *lead salt* with H_2O, and *potassium salt* (anhydrous) are described. The sulphonic acid yields *β*-sulphopyromucic acid on reduction with zinc dust in ammoniacal solution. On oxidation with bromine, it yields either sulphofumaric acid or *αα-chlorobromofurfuran-β-sulphonic acid*, as the bromine is in excess or limited (1 mol.). The latter acid forms a waxy, deliquescent mass when its aqueous solution is evaporated. The *barium salt* with H_2O, *calcium salt* with $2H_2O$, *lead salt* with H_2O, and *potassium salt* (anhydrous) are described.

JN. W.

Reactions of Dimolecular Nitriles. By P. S. BURNS (*J. pr. Chem.* [2], **47**, 105—134).—Throughout this paper the author substitutes the terms dipropionitrile and diacetonitrile for imidopropionylethyl cyanide and imidoacetylmethyl cyanide respectively (Abstr., 1889, 114). The compounds of benzoyl with dipropionitrile have been already described (Abstr., 1891, 888; 1892, 450). The compound $NBz{:}CMe{\cdot}CHBz{\cdot}CN$ (m. p. 158°) is now called dibenzoyldiacetonitrile; it and its reactions have also been described (Abstr., 1892, 450).

Benzoyldiacetonitrile, $NBz{:}CMe{\cdot}CH_2{\cdot}CN$, is prepared by mixing ethylic benzoate, sodium ethoxide, and diacetonitrile in well cooled ether and completing the reaction on the water bath; the sodium compound separates and is decomposed by water. It crystallises in long, white needles, melts at 82°, and is soluble in most solvents except dilute acids, alkalis, and water. It is isomeric with the imido-derivative (m. p. 148°) obtained by the action of ammonia on *α*-cyanobenzoylacetone (*loc. cit.*); by hydrolysis, it is decomposed into cyanacetone, ammonia, and benzoic acid.

Benzoylbenzacetonitrile, $N\leqslant\begin{matrix}CPh(OH)\\CPh\text{——}\end{matrix}\!>CH{\cdot}CN$, is the product of the action of benzoic chloride on benzacetodinitrile; it crystallises in small, silky, yellow needles, melts at 250°, and dissolves in benzene, carbon bisulphide, and acetone, but not in ether, alcohol, acids, or alkalis. It is remarkably stable and can be dissolved in strong sulphuric acid without change; it does not form salts.

Cyanacetoxime, $NOH{:}CMe{\cdot}CH_2{\cdot}CN$, is obtained by the action of hydroxylamine hydrochloride on diacetonitrile in concentrated aqueous solution; it crystallises in long needles, melts at 96°, and is soluble in ether, alcohol, hot benzene, and alkalis; its *acetyl* derivative crystallises in small prisms, and melts at 169°. Hot hydrochloric acid converts it into cyanacetone and hydroxylamine hydrochloride. When heated with water, it undergoes isomeric change, becoming *methyl-*

isoxazolonimide, $N\langle\begin{smallmatrix}-O-\\ CMe\cdot CH_2\end{smallmatrix}\rangle C{:}NH$, which forms feathery crystals, melts at 84°, and is easily soluble in water, alcohol, ether, and benzene; its hydrochloride was prepared. Hot hydrochloric acid decomposes it with formation of ammonium chloride.

Phenylisoxazolonimide, $C_9H_8N_2O$, is produced when hydroxylamine acts on benzacetodinitrile; it has been already obtained (Obrégia, Abstr., 1892, 324) by the action of hydroxylamine on cyanacetophenone in alkaline solution. Hydrochloric acid converts it into phenylisoxazolone (Abstr., 1891, 468). The *hydrochloride* and *acetyl* derivative (m. p. 164°) of the imide were prepared. In ethereal solution it absorbs 2 atoms of bromine, forming the compound

$$PhC\langle\begin{smallmatrix}N-O\\ CHBr\end{smallmatrix}\rangle CBr\cdot NH_2,$$

which is white, crystalline, and melts with decomposition at 128—130°; water converts it into the monobromo-derivative, $PhC\langle\begin{smallmatrix}N-O\\ CHBr\end{smallmatrix}\rangle CO$, which crystallises in pale yellow prisms, and melts with decomposition at 134°.

The compound $C_6H_{10}N_2O$ is produced by the action of hydroxylamine on dipropionitrile; it has been described by Hanriot (Abstr., 1892, 79) as amidomethylethylisoxazole, but the author shows cause why it should be regarded as *oximidodipropionitrile*,

$$\begin{matrix}CEt=\!=\!=N\\ |\\ CMeH\cdot C(NH)\end{matrix}\rangle O.$$

Cyanacetone hydrazone, $CN\cdot CH_2\cdot CMe{:}N\cdot NHPh$, is obtained by the action of phenylhydrazine on diacetonitrile in acetic acid; it crystallises in prismatic needles and melts at 97°; its *hydrochloride* was prepared.

Cyanacetophenone hydrazone, $CN\cdot CH_2\cdot CPh{:}N\cdot NHPh$, from benzacetodinitrile and phenylhydrazine, crystallises in prismatic needles, and melts at 121° (compare Hanriot, Abstr., 1292, 324). A. G. B.

Amidophosphates. By H. N. Stokes (*Amer. Chem. J.*, **15**, 198—214).—*Diphenylic amidophosphate*, $NH_2\cdot PO(OPh)_2$, is prepared by boiling phosphorus oxychloride (1 mol.) with phenol (2 mols.) in a reflux apparatus, and treating the alcoholic solution of the resulting product, a mixture of triphenylic phosphate, diphenylphosphoric chloride, phenylphosphoric dichloride, and unchanged oxychloride, with a slight excess of alcoholic ammonia. The crystalline amidophosphate, mixed with oily phenylic phosphates, separates on the addition of water, and is purified in the usual way. Diphenylic amidophosphate forms brilliant, colourless crystals, melts at 148°, and sublimes at 230°, with partial decomposition into phenol, ammonia, and a non-volatile substance containing phosphorus. *Phenylic hydrogen amidophosphate* is obtained in solution by decomposing *phenylic lead amidophosphate* with hydrogen sulphide. The *ammonium*, *silver*, and *barium* salts are also described. The phenylic hydrogen amido-

phosphate takes up water to form *phenylic hydrogen ammonium phosphate*, which with silver nitrate gives a crystalline precipitate of *phenylic diargentic phosphate*. *Potassium hydrogen amidophosphate* is obtained by hydrolysis of the phenylic salt with potash. The preparation and properties of numerous metallic salts are also described. The silver salt is decomposed on ignition into a stable *silver pyrimidophosphate*, $NH[PO(OAg)_2]_2$. Free *amidophosphoric acid* is obtained in solution by passing hydrogen sulphide through an aqueous suspension of the silver salt, and is precipitated by alcohol in colourless, microscopic crystals. It is sweet to the taste, and is not hydrolysed by caustic alkalis. Its alkali hydrogen salts precipitate metallic hydrogen salts from metallic solutions, and its normal alkali salts give normal metallic salts. JN. W.

Alkali Phenoxides. By DE FORCRAND (*Compt. rend.*, **116**, 192—194 and 437—439).—The author has prepared and analysed the compound C_6H_6O,KOH,H_2O or $C_6H_5{\cdot}OK,2H_2O$, obtained in brilliant lamellæ by Roméi's method of mixing and concentrating alcoholic solutions of the two constituents, and also by concentrating mixed aqueous solutions.

The compound $C_6H_6O,NaHO,4H_2O$ or $C_6H_5{\cdot}ONa,5H_2O$ is obtained in crystals by concentrating mixed aqueous solutions of the constituents; and the compound $C_6H_6O,NaOH,2H_2O$ or $C_6H_5{\cdot}ONa,3H_2O$, by Roméi's method of concentrated mixed alcoholic solutions.

When placed in a dry vacuum for several weeks, all these compounds lose water, and although they do not become completely anhydrous, the composition of the residues agrees much more closely with the formula C_6H_5MO than with the formula C_6H_6O,MOH.

It follows that Roméi's statements are incorrect, and that the so-called hydrated alkali phenates are really hydrates of the phenoxides, the general formula being $C_6H_5MO + xH_2O$. This view is supported by their thermochemical behaviour.

The heats of dissolution of the compounds $C_6H_5NaO + 3H_2O$, $C_6H_5NaO + 5H_2O$, and $C_6H_5KO + 2H_2O$ are respectively +0·94 Cal., −4·29 Cal., and +0·12 Cal. If the compounds are regarded as molecular compounds of phenol and the alkali hydroxides, these values would lead to heats of formation much too high for efflorescent hydrates, whereas the numbers calculated on the assumption that the metal has displaced the hydrogen in the hydroxyl group are of the same order of magnitude as in the case of other efflorescent hydrates. This furnishes additional evidence that the true constitution of these compounds is represented by the formula $C_6H_5MO + nH_2O$. C. H. B.

Derivatives of Dibromothymol. By F. PELLACANI (*Gazzetta*, **22**, ii, 583—586).—*Methyldibromothymol*, $C_6HMePrBr_2{\cdot}OMe$, may be prepared by the general method from dibromothymol; it is a yellow oil, which does not solidify at −18°.

Ethylenedibromothymol, $C_2H_4(O{\cdot}C_6HMePrBr_2)_2$, is obtained by the action of alcoholic potash and ethylenic bromide on dibromothymol;

it forms lustrous needles, melting at 151—153°, and is very soluble in acetic acid or light petroleum, but only sparingly so in alcohol.

Acetyldibromothymol, $C_6HMePrBr_2{\cdot}OAc$, is a syrupy, yellow oil, which does not solidify at −18°. *Benzoyldibromothymol* is obtained in minute, lustrous, colourless prisms, melting at 88—90°; it is very soluble in alcohol, light petroleum, or glacial acetic acid.

W. J. P.

Action of Chlorine on Phenols. By T. Zincke (*Ber.*, **26**, 498—512; see also Abstr., 1891, 689; this vol., i, 259).—A further examination of the acid, $C_6Cl_5H_3O_3$, obtained from pentachlororesorcinol, shows that it has the constitution

$$CHCl_2{\cdot}CO{\cdot}CCl{:}CH{\cdot}CCl_2{\cdot}COOH;$$

and therefore that pentachlororesorcinol and hexachlororesorcinol are decomposed in a similar way.

Hexachlororesorcinol, when treated with bleaching powder in acetic acid solution, yields an acid of the constitution

$$CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH.$$

A similar reaction takes place with pentachlororesorcinol, when trichloroacetyltrichlorocrotonic acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CH{\cdot}CCl_2{\cdot}COOH$, is obtained. In the absence of acetic acid, however, the pentachlororesorcinol is converted into trichloracetyl-β-chloracrylic acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CH{\cdot}COOH$. The same acid is also obtained by the action of bleaching powder on trichloracetylchlorocrotonic acid, and on the acid $C_6Cl_5H_3O_3$ obtained from pentachlororesorcinol.

Of the acids $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH$ and

$$CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH$$

obtained from hexachlororesorcinol, the first is easily converted into the second by the action of bleaching powder; but the second is very stable towards bleaching powder, and when treated with a concentrated solution, is precipitated as calcium salt. In dilute solution, however, it is slowly converted into the acid $CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COOH$, which, however, cannot be isolated, but decomposes yielding dichloromaleïc acid. If, however, the action takes place in acetic acid solution, the compound $CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_3$ is obtained, and this is identical with the substance obtained by Zincke and v. Lohr from tetrachlorodiketopentene (Abstr., 1892, 1186).

Of the acids $CHCl_2{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CCl_2{\cdot}COOH$ and

$$CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CCl_2{\cdot}COOH$$

obtained from pentachlororcinol, the former is easily converted into the latter by the action of bleaching powder. The latter acid then yields trichloracetylchloromethylacrylic acid.

The acids containing the group $CCl_2{\cdot}COOH$ are not easily converted by bleaching powder into the acid containing one carbon atom less; the group $CCl_2{\cdot}COOH$ either withstands the oxidation, or is

converted into CCl_3. If, however, these acids are first treated with soda, they are converted into $\delta\alpha$-diketonic acids, and the latter are easily oxidised (see following abstract).

Trichloracetyltrichlorocrotonic acid separates from benzene in short, colourless crystals, and melts at 96°. When treated with sodium hydroxide, it yields chloroform and an oily, uncharacteristic acid. With sodium carbonate, very little chloroform is formed, and an oily acid is obtained, which, on heating, yields the pentene derivative $C_5Cl_3HO_2$, and when oxidised with bleaching powder is converted into dichloracetyl-β-chloracrylic acid. When dissolved in acetic acid, and subjected to steam distillation, it is converted into the *ketone* $CCl_3{\cdot}CO{\cdot}CCl{:}CH{\cdot}CHCl_2$. This is a heavy, highly-refractive, yellow oil, which has a characteristic odour resembling that of camphor, boils at 122—124° under 18—20 mm. pressure, and when treated with alkali, yields chloroform and an oily acid.

Trichloracetyl-β-chloracrylic acid crystallises in white, satiny leaflets, and melts at 126°. The *methylic* salt crystallises in colourless tablets, and melts at 71°. When allowed to remain with excess of 10 per cent. soda for 24 hours, it is converted into chloroform and chloromaleïc acid, $COOH{\cdot}CH{:}CCl{\cdot}COOH$; this crystallises in white needles, sinters at 95—96°, and melts at 108°. The *potassium hydrogen* salt crystallises in rosettes of colourless needles. The *barium* salt, $C_2HCl<\begin{matrix}COO\\COO\end{matrix}>Ba,2H_2O$, crystallises in white crusts. The author has also prepared chloromaleïc acid from chlorofumaric acid, and finds that it is identical with the above acid.

Perchloracetylacrylic acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COOH$, is obtained when the acid $C_6HCl_7O_3$, from hexachlororesorcinol is treated with sodium carbonate, and then cautiously oxidised with bleaching powder. It crystallises with water, melts at 50°, when dry melts at 83—84°, and is identical with the perchloracetylacrylic acid described by Zincke and v. Lohr (Abstr., 1892, 1186).

Trichloracetylchloromethylacrylic acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}COOH$, is best obtained by treating the acid $CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CCl_2{\cdot}COOH$ (from pentachlororcinol) with sodium carbonate, and then oxidising with bleaching powder. It crystallises in colourless needles or prisms, melts at 135°, and when treated with sodium hydroxide yields chloroform and chlorocitraconic acid. E. C. R.

Conversion of the Ketochlorides of Resorcinol and Orcinol into Pentene Derivatives. By T. Zincke and O. Fuchs (*Ber.*, **26**, 513—521; compare this vol., i, 259).—The chlorinated δ-ketonic acids obtained from the ketochlorides of resorcinol and orcinol are converted into chlorine derivatives of metadikopentene by heating them with 10—15 parts of concentrated sulphuric acid, pouring the product on to ice, and then subjecting it to steam distillation. The diketopentenes are also obtained by treating the ketonic acids with sodium carbonate, allowing the faintly alkaline mixture to remain for a short time, then acidifying with hydrochloric acid and extracting with ether. On evaporating the ethereal solution, a viscid, yellow oil is obtained, which is a $\delta\alpha$-diketonic acid; this,

when cautiously heated on the water-bath, decomposes and yields the diketopentene.

The acid, $CCl_3{\cdot}CO{\cdot}CCl_2{\cdot}CHCl{\cdot}CCl_2{\cdot}COOH$, from pentachlororesorcinol, is easily converted into tetrachlorodiketopentene by boiling with water, but with soda, it yields chloroform and pentachloroglutaric acid. The other acids, with the exception of the acid

$$CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CCl_2{\cdot}COOH,$$

which yields perchloroketoindene, require to be treated as described above, but bye-products are always obtained. Thus acids containing the group $CCl_3{\cdot}CO$ yield chloroform, and the acid

$$CHCl_2{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CCl_2{\cdot}COOH$$

yields the compound C_5Cl_3MeO.

Dichlorodiketopentene, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CH{\cdot}CO\end{matrix}\!>\!CHCl$, crystallises in white, silky needles, melts at 89°, sublimes in slender needles, boils without decomposition, and when warm has a characteristic odour. It is not attacked by sodium carbonate, and yields a brownish solution with sodium hydroxide. When treated with bleaching powder in acetic acid solution, it yields trichloracetyl-β-chloracrylic acid, $CCl_3{\cdot}CO{\cdot}CCl{:}CH{\cdot}COOH$ (m. p. 126°). The *azine*, $C_{11}H_7ClN_2O$, obtained by warming an alcoholic solution of the diketone with orthophenylenediamine, crystallises from benzene in red needles, which sinter at 160°, and melt at 170° with decomposition, and from alcohol or acetic acid in slender, yellow needles, which melt at 160—165° with decomposition; both modifications give with soda a sparingly soluble, yellow salt, and with hydrochloric acid a yellow precipitate.

Unsymmetrical trichlorodiketopentene, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CH{\cdot}CO\end{matrix}\!>\!CCl_2$, crystallises in stout, colourless needles, melts at 69°, is volatile with steam, is not attacked by sodium carbonate, but is decomposed by sodium hydroxide, and yields resins with orthophenylenediamine.

Symmetrical trichlorodiketopentene, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CCl{\cdot}CO\end{matrix}\!>\!CHCl$, crystallises in colourless needles, melts at 49—50°, and closely resembles the preceding compound, but with orthophenylenediamine, yields a compound which crystallises in beautiful red needles, blackens at 185°, and melts at 190—195°.

Dichlorodiketomethylpentene, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CMe{\cdot}CO\end{matrix}\!>\!CHCl$ (see also this vol., i, 260), crystallises in thin, colourless tablets, and melts at 81°. The *azine* crystallises in slender, yellow needles, and melts at 186°.

Trichlorodiketomethylpentene, $\begin{matrix}CCl{\cdot}CO\\ \|\\ CMe{\cdot}CO\end{matrix}\!>\!CCl_2$, crystallises in short, colourless needles or prisms, melts at 64—65°, and yields resins with orthophenylenediamine.

Perchloroketoindene, $C_6Cl_4<\begin{matrix}CO\\CCl\end{matrix}>CCl$, is obtained by dissolving the acid $CHCl_2\cdot CO\cdot CCl:CCl\cdot CCl_2\cdot COOH$ in sodium carbonate, and after allowing the mixture to remain for a time, filtering off the precipitate which is formed and adding hydrochloric acid to the clear liquid. The precipitate thus obtained crystallises in yellow plates, melts at 148°, and is identical with the perchloroketoindene described by Zincke and Günther (this vol., i, 344). E. C. R.

Creosotes and Guaiacol. By A. Béhal and E. Choay (*Compt. rend.*, **116**, 197—200).—Officinal creosotes are mixtures of very variable composition. Their analysis is based on the following facts. (1) When a current of hydrogen bromide is passed into a heated mixture of creosote under ordinary pressure, the methyl derivatives are completely demethylated. (2) Phenols are volatile in water vapour, whilst polyphenols are practically non-volatile. (3) From the aqueous solution, ether completely removes catechol and homocatechol, together with any traces of phenols that may be left. (4) Catechol and homocatechol can be separated with considerable accuracy by means of benzene.

Guaiacol.—Commercial guaiacol is very impure, and rarely contains more than 50 per cent. of the pure compound. It is generally described as a liquid, but the values attached to its boiling point and sp. gr. are very various.

In order to obtain the pure compound, 58 grams of sodium is dissolved in methyl alcohol, mixed with a solution of 270 grams of catechol in methyl alcohol, and heated at 120—130° with excess of methylic iodide in an autoclave. After distilling off the alcohol, the product is distilled in a current of steam, the guaiacol dissolved in sodium hydroxide solution, and agitated with ether to remove veratrol. The guaiacol is liberated by means of hydrochloric acid, distilled in a current of steam, and afterwards fractionated. The portion boiling at 205—207° is cooled by means of methylic chloride, when the pure guaiacol crystallises. It is a white, solid compound which crystallises readily in uniaxial dihexagonal prisms; it melts at 28·5°, and boils at 205·1°. When melted, guaiacol remains indefinitely in superfusion. Its sp. gr. at 0° = 1·1534, and at 15° 1·143. It dissolves in most organic solvents, including anhydrous glycerol, but it does not dissolve in officinal glycerol. If, however, the latter is heated, the guaiacol dissolves readily, but separates as an oil on cooling. Guaiacol crystallises readily from light petroleum. It has a sweet and intensely astringent taste, but does not attack the mucous membrane. C. H. B.

Additive Products of Benzoquinone and Toluquinone. By T. H. Clark (*Amer. Chem. J.*, **14**, 553—576).—Contains the experimental data upon which some conclusions already published by Nef (Abstr., 1891, 1348; compare also 1892, 1272) are based, and an account of some further experiments. Five additive products of benzoquinone have so far been obtained; a di- and a tetra-bromide, a

di- and a tetra-chloride, and a dichloride-dibromide. These are stable, especially the chlorine derivatives. The dichloride and dibromide have a faint, quinone-like odour, are light coloured, and dissolve moderately in organic solvents, and without change in fuming nitric acid. The other three are colourless, inodorous, and very sparingly soluble in organic solvents; they dissolve with difficulty and without change in warm fuming nitric acid. All five are instantly decomposed by dilute aqueous soda; they all lose hydrogen haloïd (1 or 2 mols.) when their alcoholic solutions are warmed, and form one, or two isomeric, halogen-substituted benzoquinones. When reduced with zinc and acetic acid, they all yield quinol. Toluquinone forms a dibromide and a dichloride [$Me : O_2 : Br_2$ (or Cl_2) = 6 : 1 : 4 : 2 : 3], but no tetrahalogen additive product. These products closely resemble the corresponding benzoquinone derivatives. When reduced with zinc and acetic acid, they yield toluquinol. When their alcoholic solutions are boiled, they lose halogen hydride, and form mixtures of meta- and para-chloro- (or bromo-) toluquinone. This shows that the halogen atoms must have been added on in the 2 : 3-, and not in the 5 : 6-, positions. That the addition of 2 halogen atoms always takes place in ortho-positions is proved by the fact that benzoquinone dichloride-dibromide, formed by the successive addition of 2Cl and 2Br, yields, when warmed in alcoholic solution, a mixture of meta- and para-chlorobromoquinone [$O_2 : Cl : Br$ = 1 : 4 : 2 : 6 and 1 : 4 : 6 : 3] in about equal proportions.

The corrected melting points of the chlorine additive products are given, and differ slightly from those previously quoted. The dichloride melts at 146°, and then decomposes at about 185°, but the solid sublimes without decomposition; it was obtained in colourless, transparent plates by recrystallisation from acetic acid. The tetrachloride darkens at about 185°, and usually melts at 226°, but often sublimes without melting at 236°. The dichloride-dibromide melts at 202—203° with decomposition, part subliming at the same time. Incidentally it is mentioned that a good method of preparing the quinones is to dissolve quinol (or orthotoluidine) in dilute sulphuric acid, add manganese dioxide, distil the mixture with steam, cool the distillate with ice and salt, and filter off the solid benzo- (or tolu-) quinone.

Three substances previously mentioned (Abstr., 1891, 1348) are also more accurately described. *Chlorobromaniline* [$NH_2 : Cl : Br$ = 1 : 2 : 5] crystallises from water in fine, silky, white needles melting at 44·5°. Its *hydrochloride*, $C_6H_5ClBrN,HCl + H_2O$, melting at 196°, and *sulphate*, $(C_6H_5ClBrN)_2,H_2SO_4$, were prepared. *Bromochloroparanitrophenol* [$OH : Cl : NO_2 : Br$ = 1 : 2 : 4 : 6] forms white crystals melting at 139·5°. When reduced with tin and hydrochloric acid, it yielded *bromochloroparamidophenol stannochloride* as long, silky, white needles melting at 228°. The sulphate forms white, silky needles melting at 221°, and the base itself long, colourless needles, but neither of these was obtained quite pure.

Toluquinone dichloride, obtained by passing chlorine into a chloroform solution of the quinone, is a white, crystalline substance which melts at 135—136°, and then decomposes at about 164°, but can also

be sublimed unchanged. The *dibromide* forms pale yellow crystals, melting at 61—62°, and subliming at a higher temperature.

The action of hydrochloric acid on benzoquinone does not give rise to a hydrochloride. When the dry gas is passed into a chloroform solution of the quinone, the following reactions occur; the hydrochloric acid first reduces the quinone, setting free chlorine, which remains dissolved, and forming quinol, which at once combines with unchanged quinone to form quinhydrone; the latter is then attacked by more hydrochloric acid, which reduces the quinone part of it to quinol, setting more chlorine free. The whole of the chlorine set free now attacks the quinol which has been formed, and converts it into chloroquinol, which is obtained as the sole final product of the reaction. In the case of toluquinone, the reaction is similar, and a mixture of much para- with some meta-chlorotoluquinol is obtained.

Quinhydrone, when heated in chloroform solution with dry gaseous hydrogen chloride, yields a mixture of quinol and chloroquinol in molecular proportion. A *chloroquinhydrone*, $C_6H_4(OH)_2,C_6H_3ClO_2$, may be obtained by mixing ethereal solutions of quinol and chloroquinone; it is readily decomposed by solvents. Quinone and chloroquinol do not, however, yield a similar compound; as a result of mixing their ethereal solutions, much chloroquinol and quinone, and some quinol and chloroquinone, were obtained. C. F. B.

Some Derivatives of Chloranil. By H. S. Grindley and C. L. Jackson (*Ber.*, **26**, 397—398).—If chloranil is treated with sodium phenoxide, *diphenoxydichloroquinone*, $C_6Cl_2O_2(OPh)_2$, is obtained in red needles melting at 242°. When reduced with hydriodic acid, this substance yields the corresponding *quinol* in white needles melting at 197°. When treated with ethylic sodiomalonate, a blue precipitate is obtained, changing to yellow when the solution is acidified. The yellow substance, which crystallises in needles, is a molecular compound, $C_6Cl_2O_2,2CH(COOEt)_2$; it is reduced by hydriodic acid to a white substance, probably the quinol. The blue substance is its *sodium* derivative, $C_6Cl_2O_2,2CNa(COOEt)_2$. C. F. B.

Mercuranilido-compounds. By A. Piccinini and G. Ruspaggiari (*Gazzetta*, **22**, ii, 604—610).—The double hydrochloride of mercurophenylamine and aniline prepared by Pesci (Abstr., 1892, 1448) was stated by him to be identical with a compound obtained in another way by Gerhardt and by Schiff. The authors now establish the identity of the products from the two sources, showing that they yield the same substance when heated with water; this remains as a yellowish, insoluble powder having the composition

$$2NPhHg,HCl,HgCl_2;$$

on treatment with hydrogen sulphide, it yields aniline hydrochloride, mercuric sulphide, and hydrochloric acid.

The substance prepared by Schiff, by the action of aniline on mercuric acetate solution, yields mercurophenylamine acetate when treated with water; it must therefore be considered as a double

acetate of mercurophenylamine and aniline having the composition $NH_2Ph,C_2H_4O_2,NPhHg,C_2H_4O_2$.

A substance to which the formula $2NH_2Ph,Hg(NO_3)_2$ has been assigned, is obtained by the action of aniline on mercuric nitrate in aqueous solution; on treating it with boiling water, a compound of the composition $N_2H_2Ph_2,Hg_2(NO_3)_2$ is supposed to be formed. The authors find, however, that the former substance should be considered as a double salt of aniline and mercurophenylamine, as on boiling with water it yields mercurophenylamine nitrate; they conclude, further, that all the supposed mercuranilido-compounds are really double salts of aniline and mercurophenylamine. W. J. P.

Direct Conversion of Aniline into Nitrobenzene. By PRUD'HOMME (*Bull. Soc. Chim.* [3], **7**, 621—623; compare Bamberger and Meimberg, next abstract).—When a mixture of aniline, hydrogen peroxide, and water, with or without the addition of magnesia, is heated in a reflux apparatus, the principal products are paramidophenol, azobenzene, azoxybenzene, and nitrobenzene.

Azobenzene and azoxybenzene are not converted into nitrobenzene when similarly treated with hydrogen peroxide. A. R. L.

Direct Conversion of Aniline into Nitrobenzene. By E. BAMBERGER and F. MEIMBERG (*Ber.*, **26**, 496—497; compare Prud'homme, preceding abstract).—When potassium permanganate (120 grams) dissolved in water (3 litres) is gradually dropped into a solution of aniline (8 grams) in water (360 grams) at 0°, the mixture being kept in agitation for 8—9 hours, and filtered, ether extracts a brown oil. On distilling the latter in a current of steam, nitrobenzene and azobenzene (but no nitrosobenzene) pass over, and an unknown compound melting at 226° remains. The amounts of the products are small.

By reducing an alkaline solution of diazobenzene with stannous oxide at −10°, hydrazobenzene and phenylhydrazine are formed.

A. R. L.

Action of Phosphorus Oxychloride and of Phosphorus Thiochloride on Aromatic Amines. By P. RUDERT (*Ber.*, **26**, 565—575).—*Phosphoric orthotoluidide*, $PO(NH\cdot C_6H_4Me)_3$, is formed by the action of phosphorus oxychloride on orthotoluidine. It crystallises in colourless, or reddish, needles or plates, melts at 225°, is decomposed by boiling concentrated hydrochloric acid or soda, and is very readily acted on by oxidising agents. The *bromo*-derivative, $PO(NH\cdot C_6H_3MeBr)_3$, crystallises in slender, almost colourless needles, and melts at 253°. The *nitro*-derivative, $PO(NH\cdot C_6H_3Me\cdot NO_2)_3$, is a pale yellow, crystalline powder, but it was not obtained in a pure condition.

Diorthotoluidophosphoric acid, $OH\cdot PO(NH\cdot C_6H_4Me)_2$, is obtained when orthotoluidine is treated with excess of phosphorus oxychloride; it is a colourless, crystalline powder, melts at 95°, and is decomposed into toluidine and phosphoric acid by hot concentrated hydrochloric acid. The *sodium* salt crystallises in colourless needles. The *barium* and *silver* salts crystallise in needles.

Thiophosphoric orthotoluidide, $PS(NH\cdot C_6H_4Me)_3$, can be obtained by treating orthotoluidine with phosphorus thiochloride; it crystallises in colourless needles, melts at 134·5°, and is decomposed by nitric acid, bromine, and boiling concentrated hydrochloric acid.

Phosphoric paratoluidide, $PO(NH\cdot C_6H_4Me)_3$, crystallises in colourless prisms, which belong to the triclinic system, and become opaque on keeping, probably owing to a change in crystalline form; it melts at 192° and is only slowly acted on by hot concentrated hydrochloric acid and by oxidising agents. The *bromo*-derivative, $PO(NH\cdot C_6HMeBr_3)_3$, is formed when phosphoric paratoluidide is treated with bromine in glacial acetic acid solution until a permanent coloration is produced and the mixture then warmed; it crystallises in lustrous, colourless needles, turns brown at about 100°, and melts at about 180°. The *bromo*-derivative, $PO(NH\cdot C_6H_3MeBr)_3$, is produced when the preceding compound is boiled with glacial acetic acid; it crystallises in very slender, colourless needles, melts at 221°, and is decomposed by nitric acid. The *nitro*-derivative, $PO(NH\cdot C_6H_3Me\cdot NO_2)_3$, crystallises in small, lemon-yellow needles, melts at 247°, and explodes when heated more strongly.

Diparatoluidophosphoric acid, $OH\cdot PO(NH\cdot C_6H_4Me)_2$, is a crystalline, colourless powder melting at 124°. The *barium* and silver salts crystallise in colourless needles.

Thiophosphoric paratoluidide, $PS(NH\cdot C_6H_4Me)_3$, crystallises in colourless needles, melts at 185°, and is converted into derivatives of phosphoric paratoluidide on treatment with bromine or with nitric acid.

Phosphoric α-naphthalide, $PO(NH\cdot C_{10}H_7)_3$, prepared by treating α-naphthylamine with phosphorus oxychloride, crystallises in colourless needles, melts at 216°, and is decomposed by hot concentrated hydrochloric acid; when excess of phosphorus oxychloride is used in the above reaction, *dinaphthylamidophosphoric acid*, $OH\cdot PO(NH\cdot C_{10}H_7)_2$, is formed, and can be isolated in the form of a brownish, crystalline powder melting at 197°.

Phosphoric β-naphthalide, $PO(NH\cdot C_{10}H_7)_3$, crystallises in colourless plates, and melts at 170°; *dinaphthylamidophosphoric acid*, prepared from β-naphthylamine, is a light orange powder, and melts at 150°.

Phosphoric ethylanilide, $PO(NEtPh)_3$, can be obtained by heating ethylaniline with phosphorus oxychloride; it crystallises in slender, colourless needles, and melts at 149°. F. S. K.

Oxidation Products of Alkyl Derivatives of Orthodiamines. By F. KEHRMANN and J. MESSINGER (*Ber.*, **26**, 599—600).—This paper is purely controversial, being a reply to Fischer and Heiler (this vol., i, 266). F. S. K.

Interaction of Orthamidoditolylamine and Alloxan Derivatives. By O. KÜHLING (*Ber.*, **26**, 540—545).—The author has previously shown that orthodiamines react with alloxan and its derivatives with formation of azines, and has now investigated the action of orthodiamines in which a hydrocarbon radicle is substituted for one of the hydrogen atoms of the amido-group, in order to ascertain whether substances corresponding to Witt's azonium

bases are formed. The results obtained show that the reaction in this case proceeds in a different manner.

When alloxan is mixed with orthamidoditolylamine,

$$NH_2{\cdot}C_7H_6{\cdot}NH{\cdot}C_7H_7$$

(Abstr., 1892, 853), in alcoholic solution and allowed to remain at the ordinary temperature, only the central carbonyl group enters into the reaction, with formation of *alloxanylorthamidoditolylamine*, $C_7H_7{\cdot}NH{\cdot}C_7H_6{\cdot}N{:}C<\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}>CO$, which forms glittering, yellow prisms, melts with decomposition at 252°, and dissolves in concentrated sulphuric acid with a deep red colour. If the alcoholic solution of alloxan and orthamidoditolylamine be boiled with an excess of fuming hydrochloric acid, a second molecule of alloxan enters into combination without elimination of water, forming *dialloxanylorthamidoditolylamine*,

$$CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>C(OH){\cdot}N(C_7H_7){\cdot}C_7H_6{\cdot}N{:}C<\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}>CO;$$

it crystallises in very small, pointed needles, blackens at 300°, and is scarcely soluble in the common solvents, but readily dissolves in solutions of the alkalis and their carbonates; none of its salts could, however, be isolated. It dissolves in concentrated sulphuric acid with a deep blue colour, which, on dilution, passes through red to yellow.

Dimethylalloxan yields with orthamidoditolylamine two derivatives which correspond in properties with their lower homologues.

H. G. C.

Decomposition of Diazo-compounds. By I. Remsen and P. J. Dashiell (*Amer. Chem. J.*, **15**, 105—125; compare Abstr., 1887, 136; 1888, 268; 1889, 975).—It has already been noted (Abstr., 1887, 136) that the chief product of the action of alcohol on paradiazotolueneorthosulphonic acid is not tolueneorthosulphonic acid, but ethoxytolueneorthosulphonic acid, and that the higher the pressure, the larger the proportion of the ethoxy-derivative formed. The authors have further studied this reaction from three points of view, as follows:—(1) The pressure was constant (300 mm.) and the strength of alcohol varied. The presence of small quantities of water in the alcohol has little influence on the course of the reaction in the decomposition of the diazo-compound. The presence of more than 15 per cent. of water gives rise to other reactions than those involved in the formation of toluenesulphonic acid and ethoxytoluenesulphonic acid. Typical figures from which these conclusions may be drawn are:—

Per cent. alcohol	Absolute	95·0	90·0	85·0
Per cent. of ethoxy-product..	43·4	35·8	47·7	40·9

The decomposition is more rapid in dilute alcohol. (2) The alcohol was of constant strength (absolute) and the pressure varied. The following figures were obtained.

Pressure in mm...	120	210	300	400	500	600	700	800
Ethoxy - product, per cent.....	37·2	40·6	43·4	48·7	52·8	57·7	63·2	69·8

The curve embodying these results approximates very nearly to a parabola. The experiments were conducted in a flask provided with a valve, weighted to lift at the desired pressure, and a manometer; the temperature of the flask was quickly raised until the manometer indicated the desired pressure [which must therefore be in excess of the barometric pressure, although this is not specifically stated.—ABSTRACTOR]. (3) The influence of temperature. The temperature of the above experiments would be that at which the alcohol boils under the pressure maintained. When the pressure was exerted by nitrogen, it was found that for decomposition at any given pressure, a definite temperature is necessary, and this temperature lies very near the point at which the alcohol boils at that pressure. It thus becomes uncertain whether the regular differences noted in the experiments under the various conditions are to be ascribed to the influence of temperature or pressure.

The separation of the tolueneorthosulphonic acid and ethoxytolueneorthosulphonic acid was effected by means of their barium salts, the former of which is but little soluble in boiling alcohol.

A. G. B.

Behaviour of Diazobenzene towards Potassium Ferricyanide. By E. BAMBERGER and L. STORCH (*Ber.*, **26**, 471—481).—*Nitrosobenzene*, $C_6H_5{\cdot}NO$, is obtained by cautiously running a freshly prepared solution of diazobenzene chloride into an alkaline solution of potassium ferricyanide, and allowing the mixture to remain for 70—80 hours at 0°. The compound forms colourless, translucent prisms belonging probably to the monoclinic system, melts at 67·5—68° to an emerald-green liquid which subsequently resolidifies to colourless crystals. It is volatile with steam and other vapours, has an odour recalling that of the ethereal thiocarbimides or, still more, that of cyanic acid, and yields green solutions; indeed it has already been obtained in solution (see Baeyer, this Journal, 1875, 452; Aronheim, Abstr., 1879, 651).

When the above-mentioned mixture is allowed to remain longer than 70—80 hours, a precipitate separates, which is collected and distilled with steam, when nitrosobenzene and azobenzene pass over. A further quantity of nitrosobenzene, together with nitrobenzene and diphenyl, is extracted by ether from the filtrate; the latter is then saturated with carbonic anhydride, and cautiously treated at 0° with sufficient 30 per cent. sulphuric acid to cause it to just turn Congo paper blue. Ether extracts from this solution *benzenediazoic acid*, $C_6H_5{\cdot}N_2O_2H$, a compound melting at 46—46·5° and exploding at 97—98° (see also next abstract).

The solution freed from benzenediazoic acid is treated with 50 per cent. sulphuric acid, and the precipitate, after drying on a tile, dissolved in alcohol and ether added. The precipitate which falls is dissolved in water and the solution neutralised with barium carbonate,

when barium ferrocyanide is obtained. After removing the latter, barium phenylferrocyanide, $Ba_3(PhFeC_6N_6)_2 + 2H_2O$, is isolated. A solution of this salt gives off the odour of isonitriles on being warmed with alkali, and yields precipitates with the salts of those metals which are precipitated by potassium ferrocyanide. A. R. L.

Behaviour of Diazobenzene towards Potassium Permanganate. By E. Bamberger and K. Landsteiner (*Ber.*, **26**, 482—495).—In studying the action of potassium permanganate on diazobenzene, it is necessary to employ a large excess of alkali, and to cool well. When a solution of a salt of diazobenzene (from 20 grams of aniline) is mixed with a cooled 20 per cent. solution of potassium hydroxide (60 grams), potassium permanganate (34 grams) dissolved in water (850 c.c.) added, and the mixture set aside at 0° for two days, benzenediazoic acid (last abstract) is the chief product, but there is also formed nitrosobenzene, nitrobenzene, diphenyl, azobenzene, and phenylisonitrile. The following salts of benzenediazoic acid are described. The *silver* salt is an explosive crystalline precipitate, stable towards light; the *lead* salt resembles it, and is not very soluble in hot water; the *barium* salt crystallises with 2 mols. H_2O; and the *potassium* salt forms radiating groups of needles; the *phenylhydrazine* salt melts at 94·5—95°.

When the acid is heated in an oil-bath, as soon as the temperature rises to 97—98°, decomposition suddenly takes place, the products being nitrogen, carbonic and nitrous anhydrides, nitrosobenzene, ortho- and para-nitraniline, and ortho- and para-nitrophenol. The acid is also decomposed by boiling its solution in toluene. Mineral acids decompose it at 0°, yielding principally orthonitraniline; it also decomposes when boiled with water. It is, on the other hand, very stable towards alkalis, but on being heated with aqueous potash at 280—290°, aniline distils over. On reduction with zinc-dust and acetic acid, diazobenzene is the main product, but aniline, ammonia, diphenyl, and perhaps azobenzene are also formed. The non-formation of phenylhydrazine, on reduction, leads the authors to the view that benzenediazoic acid is constituted similarly to Franchimont's nitrosamines, but although, of the two tautomeric formulæ proposed, namely, $C_6H_5{\cdot}NH{\cdot}NO_2$ and $C_6H_5{\cdot}N{:}NOOH$, their results favour the first, neither can be regarded as established. The authors also consider that their results prove that diazobenzene is a tautomeric compound which can equally well be represented by either of the formulæ $C_6H_5{\cdot}N{:}NOH$ or $C_6H_5{\cdot}NH{\cdot}NO$. A. R. L.

Reduction Products of Azo-compounds. II. By P. Jacobson, F. C. Fertsch, and W. Fischer (*Ber.*, **26**, 681—688). **III.** By P. Jacobson, F. Henrich, and J. Klein (*Ber.*, **26**, 688—698). **IV.** By P. Jacobson (*Ber.*, **26**, 699—705; see also Abstr., 1892, 839).—The base obtained as the chief product of the reduction of benzeneazophenetoïl with stannous chloride and hydrochloric acid, and obtained by Bohn from benzenehydrazophenetoïl, has been subjected to a further examination. Of the two possible formulæ, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$ [NH : NH_2 = 1 : 2], orthamidophenylpara-

phenetidine, and $NH_2{:}C_6H_3(OEt)NHPh$ [NHPh : NH_2 : OEt = 1:2:5], metanilidoparaphenetidine, the latter is proved to be the correct one, by comparing the properties of the base with these two compounds, synthetically prepared.

When the base is heated in a sealed tube with hydrochloric acid at 120—130° for three hours, it yields aniline, ethyl chloride, and ammonia.

Orthamidophenylparaphenetidine is easily obtained by heating orthobromonitrobenzene with phenetidine and alcohol in a sealed tube at 180°, and then reducing the nitrophenylphenetidine thus obtained with stannous chloride and hydrochloric acid. *Orthonitrophenylparaphenetidine*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, forms beautiful orange-yellow, prismatic crystals, and melts at 84°.

Metanilidoparaphenetidine is obtained from 2 : 5-nitrochlorodiphenylamine. When this nitro-compound is heated with sodium ethoxide and alcohol in a sealed tube at 120°, and the product diluted with water, about 15 per cent. of *metanilidoparanitrophenetoïl* is obtained; this crystallises in beautiful orange-yellow needles, and melts at 106—106·5°. A further addition of water causes a precipitate of *dianilidoazoxyphenetoïl*, $ON_2[C_6H_3(OEt){\cdot}NHPh]_2$, which crystallises in bright golden-yellow needles, and melts at 125°. Finally, the alkaline alcoholic solution in which the addition of water causes no further precipitate contains *metanilidoparanitrophenol*, $OH{\cdot}C_6H_3(NO_2){\cdot}NHPh$; this is the main product of the reaction, and is precipitated on acidifying with sulphuric acid. It crystallises from alcohol in nodular aggregates, from benzene in lustrous leaflets, melts at 165°, and is easily converted into metanilidoparanitrophenetoïl by boiling with ethylic bromide and sodium ethoxide. When heated with alcoholic ammonium sulphide at 120°, it yields metanilidoparaphenetidine.

Orthamidophenylparaphenetidine and metanilidoparaphenetidine, as also their hydrochlorides, cannot be distinguished from each other; both crystallise in colourless needles which turn violet on exposure to air, and melt at 95°. The hydrochlorides are easily soluble in water, and are precipitated by hydrochloric acid. They are distinguished by the following properties:—Orthamidophenylparaphenetidine gives, with a small quantity of ferric chloride, an intense red coloration, and a brown precipitate on the addition of a further quantity of ferric chloride; the colour is unaltered by hydrochloric acid. The *azimide* crystallises from petroleum in spears, and melts at 95—96°. The *methenyl compound* crystallises in tablets, and melts at 79—80°. The *azonium base* obtained by condensation with benzile sinters at 170°, melts at 175—180°, and yields a dark reddish-brown solution with concentrated sulphuric acid. When heated with carbon bisulphide on the water-bath, it remains unaltered, but when heated under pressure at 150°, it yields a compound which crystallises in small tablets, and melts at 227°. Metanilidoparaphenetidine, on the other hand, gives a reddish-violet coloration with ferric chloride which turns bluish-violet on the addition of hydrochloric acid. The *azimide* crystallises from petroleum in plates, and melts at 107°. The *methenyl compound* crystallises in plates, and melts at 77°. The *azonium base* melts at

144—147°, and then solidifies and melts again at 164—165°, and yields a bright red solution with concentrated sulphuric acid. When heated with carbon bisulphide on the water-bath, it is easily converted into a product which crystallises in long, white needles, and melts at 228°.

The reduction of benzeneazophenetoïl results in the production of about 50 per cent. of metanilidoparaphenetidine, 25 per cent. of aniline and paraphenetidine; and, besides this, about 5 per cent. of parethoxyparamidodiphenylamine has been isolated from the product.

Parethoxyparamidodiphenylamine is obtained as the stannochloride when the mother liquors of the preceding base are allowed to remain some time. The *free base* crystallises in beautiful colourless needles, darkens quickly on exposure to air, and melts at 98—99·5°. It gives an intense blue coloration with ferric chloride which disappears on the addition of concentrated hydrochloric acid; with a small quantity of nitrous acid, a dark violet coloration; and with more nitrous acid, a clear, golden-yellow solution. The *hydrochloride*, $C_{14}H_{16}N_2O,HCl$, crystallises in colourless needles, and is not precipitated by hydrochloric acid. The *monacetyl derivative*, obtained by boiling the base with glacial acetic acid, crystallises in slender, interlacing needles, and melts at 134°. The *diacetyl derivative* crystallises in right-angled plates, and melts at 175—176°. The *diazochloride*, $C_{14}H_{14}N_3OCl$, crystallises in bright yellow leaflets, is very stable, and in small quantities may be recrystallised from hot water without decomposition. The *thiocarbamide*, obtained by heating an alcoholic solution of the base with carbon bisulphide, crystallises in yellowish-grey needles, and melts at 155—156°. The *monobenzylidene derivative*,

$$C_{14}H_{14}NO{\cdot}N{:}CHPh,$$

melts at 109—110°.

The base has also been prepared synthetically from parahydroxydiphenylamine; both methods of preparation yield identical compounds.

Parahydroxydiphenylamine is obtained by Calm's method by heating a mixture of quinol, aniline, and calcium chloride at 250—260° (*Ber.*, **16**, 2799; **17**, 2431).

Parethoxydiphenylamine crystallises in long, flat, colourless needles, melts at 73—74°, boils at 348°, and dissolves in concentrated hydrochloric acid, yielding a hydrochloride which is easily decomposed by water. The *nitrosoamine* crystallises in short, transparent prisms, and melts at 73—75°.

Parethoxyparanitrosodiphenylamine, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO$, obtained by molecular change from the above nitrosamine, crystallises in beautiful green leaflets, and melts at 150—155°. When reduced with alcoholic ammonium sulphide, it yields parethoxyparamidodiphenylamine.

The preceding researches show that when benzenazophenetoïl is reduced with a warm mixture of stannous chloride and hydrochloric acid, about 25 per cent. of the azo-compound is resolved into aniline and paraphenetidine; the greater part, however, is reduced to the

hydrazo-compound, and this undergoes molecular change yielding two compounds, derivatives of ortho- and of para-amidodiphenylamine. It is proposed to call this reaction the *semidine reaction*, and to designate the orthamidodiphenylamine bases thus obtained by the name *orthosemidines;* the paramidodiphenylamine bases by the name *parasemidines.*

An examination of the behaviour of the five isomeric monomethyl derivatives of benzeneazophenetoïl, when treated with a warm mixture of stannous chloride and hydrochloric acid, has led to the following results:—Benzeneazoorthocresetoïl and metatoluenazophenetoïl behave in the same way as benzeneazophenetoïl, and yield as chief products an orthosemidine, a small quantity of a parasemidine, and are partly resolved into their constituents. Benzeneazometacresetoïl and orthotolueneazophenetoïl are partly resolved into their constituents, but the chief product is a parasemidine, and no orthosemidine is formed. The production of an orthosemidine is not, however, impossible, but would lead to the production of a compound containing three substituents in the ortho-position to one another. Paratolueneazophenetoïl is completely split up into paratoluidine and paraphenetidine, although the hydrazo-compound obtained from it by reduction with ammonium sulphide, when treated, in alcoholic solution, with stannous chloride and hydrochloric acid, gives a good yield of the orthosemidine. The ease with which paratolueneazophenetoïl is resolved into its constituents is not determined by the presence of two substituents in the para-position to the azo-group, for paratolueneazoorthocresetoïl, under the same conditions, behaves like benzeneazophenetoïl, and gives a good yield of the orthosemidine. The benzyl ether of paratolueneazophenol, $C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_4{\cdot}O{\cdot}CH_2Ph$, like paratolueneazophenetoïl, is also completely resolved into toluidine and the benzyl ether of paramidophenol.

Not only the position of the substituents, but also their nature, has a marked influence on the course of the reaction. When the para-position is occupied by an indifferent group, the semidine reaction takes place. When strongly electronegative or electropositive groups are present, diphenyl derivatives are obtained. Thus, parachlorohydrazobenzene yields a very small quantity of the orthosemidine, but no definite results could be obtained as to the nature of the main product of the reaction. Paraiodoazobenzene yields iododiamidodiphenyl, $NH_2{\cdot}C_6H_3I{\cdot}C_6H_4{\cdot}NH_2$. Paracetylamidohydrazobenzene yields a large quantity of paracetyldiamidodiphenylamine,

$$NHAc{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2;$$

and, finally, paradimethylamidoazobenzene yields aniline, amidodimethylaniline, and the diphenyl derivative

$$NMe_2{\cdot}C_6H_3(NH_2){\cdot}C_6H_4{\cdot}NH_2.$$

E. C. R.

Action of Sodium Sulphide on Orthodiazophenol Chloride. By A. Purgotti (*Gazzetta*, **22**, ii, 614—620; compare Tassinari, Abstr., 1892, 1316).—On slowly adding orthodiazophenol chloride

solution to sodium sulphide solution, considerable evolution of gas occurs; after heating on the water-bath and adding hydrochloric acid, a black, viscous mass separates, and is washed with dilute soda. By a somewhat lengthy process of purification, a *compound* is finally isolated which crystallises in long, silky needles melting at 127°, and has the constitution $S(S\cdot C_6H_4\cdot OH)_2$ (?). It gives the normal molecular weight by the cryoscopic method in acetic acid solution, and is very soluble in alcohol, ether, acetic acid, chloroform, ethylic acetate, or acetone, sparingly so in benzene, and insoluble in water. It dissolves in alkalis with formation of metallic derivatives whose solutions give precipitates with silver, lead, mercury, copper, zinc, and cadmium salts. It gives orthohydroxyphenyl mercaptan on reduction with zinc and sulphuric acid, and, when treated with acetic anhydride, yields *orthodiacetoxytrithiobenzene*, $S(S\cdot C_6H_4\cdot OAc)_2$, as a yellowish, viscous mass. W. J. P.

Diazoamidobenzene and Paradiazoamidotoluene Benzoates and Metanitrobenzoates. By A. Haller and A. Guyot (*Compt. rend.*, **116**, 353—355).—When an alcoholic solution of benzoic or metanitrobenzoic acid and aniline or toluidine is mixed with amylic nitrite, the following reactions take place:—(*a*) $Ph\cdot COO\cdot NH_2Ph + HNO_2 = Ph\cdot COO\cdot N_2Ph + 2H_2O$; (*b*) $Ph\cdot COO\cdot N_2Ph + Ph\cdot NH_2 = Ph\cdot COO\cdot NH_2Ph\cdot N_2Ph$. The same products are obtained when amylic nitrite is added in only half the quantity indicated by the equation.

Diazoamidobenzene benzoate, $Ph\cdot COO\cdot NH_2Ph\cdot N_2Ph$, crystallises from ether in yellow needles which alter rapidly if not quite free from nitrite, but are much more stable when pure, although they become brown after some time; they melt at 91°, and are soluble in almost all the ordinary solvents. *Diazoamidobenzene metanitrobenzoate* forms yellow crystals which melt at 90° and dissolve in all the usual solvents except light petroleum. *Paradiazoamidotoluene benzoate* crystallises from ether in long, yellow needles. *Paradiazoamidotoluene metanitrobenzoate* forms yellow needles which alter rapidly. When heated with dilute hydrochloric acid, it yields paratoluidine hydrochloride, metanitrobenzoic acid, and paracresol, which proves that these compounds are really diazoamido-derivatives.

Attempts to prepare the acetate, formate, and orthotoluate of diazoamidobenzene gave negative results, crystallised diazoamidobenzene being always formed. The action of amylic nitrite on a mixture of paratoluidine and ethylic cyanacetate or acetoacetate yields only diazoamidotoluene. C. H. B.

Oxidation of Acid Hydrazides by Fehling's Solution. By H. Strache and S. Iritzer (*Monatsh.*, **14**, 33—38).—It has been shown by Tafel, Gattermann, and others (Abstr., 1892, 710, 843, 981) that when acid hydrazides are oxidised by means of copper acetate or ammoniacal copper solution they are converted into the corresponding derivatives of diphenylhydrazine. The authors find that if the hydrazides are treated with boiling Fehling's solution, the whole of the nitrogen is evolved in the free state. This is the case not only with the hydrazides of phenylhydrazine itself, but also with

those obtained from its homologues. Of the compounds examined, the only one hitherto unknown was the *hydrazide of stearic acid*, $C_{17}H_{35}CO{\cdot}NH{\cdot}NHPh$, which was prepared by heating the acid with an excess of phenylhydrazine to incipient boiling; it crystallises in white plates having an unctuous touch, and melts at 105—107° (corr.).

H. G. C.

Action of Bromine on Dihydrobenzaldoxime. By A. Einhorn and F. K. de Norwall (*Ber.*, **26**, 623—625).—A *dibromo*-compound of the composition $C_7H_9Br_2NO$ is obtained when dihydrobenzaldoxime (compare Einhorn and Eichengrün, Abstr., 1891, 65) is treated with a slight excess of bromine in well-cooled chloroform solution; it forms well-defined, forked crystals, melts at 122°, and decomposes with explosive violence at higher temperatures. It is decomposed by boiling hydrobromic acid with formation of benzaldehyde, and, although insoluble in alkalis and alkali carbonates, it is very readily decomposed by sodium carbonate in dilute alcoholic solution yielding carbonic anhydride, hydrogen bromide, and a very unstable compound, the nature of which was not ascertained; it liberates iodine from an alcoholic solution of potassium iodide. It would seem from these reactions that the bromo-derivative is a salt of the constitution represented by the formula $CH\begin{matrix}CH\cdot CH\\ CH_2\cdot CH_2\end{matrix}C{\cdot}CH{:}NOBr,HBr$.

When β-benzaldoxime is treated with bromine in ice-cold chloroform solution, it is converted into β-benzaldoxime hydrobromide, the yield of which is, however, barely 50 per cent. F. S. K.

Action of Benzenesulphonic Chloride on Amidoximes. By J. Pinnow (*Ber.*, **26**, 604—606; compare Abstr., 1892, 461).—Phenylethenylamidoximebenzenesulphone is decomposed by boiling water yielding benzylcarbamide, benzenesulphonic acid, phenylethenylamidoxime, and ammonia, a fact which shows that the sulphone is an intermediate product in the conversion of phenylethenylamidoxime into benzylcarbamide, under the conditions previously stated (*loc. cit.*).

Ethenylamidoximebenzenesulphone, $NH_2{\cdot}CMe{:}NO{\cdot}SO_2Ph$, prepared by treating ethenylamidoxime with benzenesulphonic chloride as previously described, melts at 130°, and is decomposed by boiling water yielding benzenesulphonic acid, acetic acid, and ammonia.

F. S. K.

Acid Salts and Constitution of Rosanilines. By A. Rosenstiehl (*Compt. rend.*, **116**, 194—197).—It is difficult to determine the exact constitution of the acid salts of the rosanilines when prepared from aqueous solutions, because the complete expulsion of the water is accompanied by a loss of acid. If, however, the dry colouring matter is subjected to the action of a current of dry hydrogen chloride or hydrogen bromide, mixed, if necessary, with air in order to moderate the reaction, absorption takes place with development of heat. If the products are allowed to remain in a vacuum over sulphuric acid for a few days, they acquire a constant weight. The polyacid salts thus obtained have not the metallic lustre characteristic of

the original colouring matter; their aqueous solutions have the colour of the parent substance, but if the salts are exposed to moist air until they deliquesce, the colour of the liquid is then different. The poly-acid salts of rosaniline decompose spontaneously, but the methyl derivatives seem to be more stable.

The compounds analysed were rosaniline hydrochloride (C_{19}), rosaniline hydrobromide (C_{19}), hexamethylrosaniline hydrochloride, hexamethylrosaniline hydrobromide, tetramethyldiamidotriphenylcarbinol hydrochloride, and tetramethylamidotriphenylcarbinol hydrobromide. In the first four cases, the quantity of halogen present agreed closely with that calculated on the assumption that 4 atoms of the halogen are present in the molecule, and in the last two compounds, with the assumption that 3 atoms of the halogen are present in the molecule.

It follows that rosaniline and its congeners have both an alcoholic and a basic function with reference to acids, the former dominating, but being modified by the presence of the amido-groups. The compounds are intermediate between alkaline bases and alcohols. The colouring matters of the rosaniline group are ethereal salts formed from tertiary amido-alcohols of the benzene series. C. H. B.

Spectro-photometric Investigation of the Salts of Aromatic Bases. By A. Weigle (*Zeit. physikal. Chem.*, **11**, 227—247).—By means of photometric measurements, the author has examined the behaviour towards hydrochloric acid of some bases, which are either themselves colourless and form coloured salts, or are themselves coloured and form colourless salts. The first base examined was rosaniline. From the results, the amounts of mon-acid and tri-acid salts present in the solution were calculated, and it was then found that the sum of the two does not equal the total quantity of rosaniline present in each case. It must therefore be assumed that in these solutions there is, in addition to the above two coloured salts, a colourless compound, and it is highly probable that this compound is a di-acid salt of rosaniline. The nitranilines, nitrotoluidines, and three of the nitronaphthylamines were also examined. It was found that the salts which are most stable towards water are formed by those bases which contain the nitro- and amido-groups in the meta-position relatively to one another; the least stable salts are formed when these groups occupy the ortho-positions, and the para-compounds are intermediate in stability.] H. C.

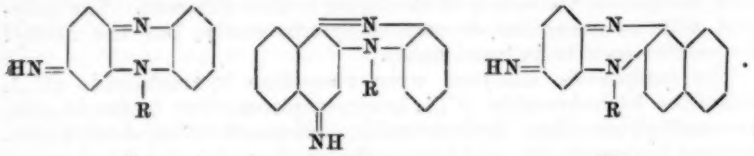
The Induline Group. By O. Fischer and E. Hepp (*Annalen*, **272**, 306—354).—The authors propose that the indulines should now be systematically classed in four groups, in the following manner.

I. *Benzenecindulines.*—These compounds may be regarded as derivatives of phenazine, and their constitution may be represented by the general formula I (next page).

II. *Rosindulines*, or derivatives of $\alpha\beta$-naphthaphenazine: the members of this class are of the general type represented by the formula II (next page).

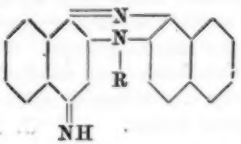
III. *Isorosindulines*, or derivatives of the yet unknown $\alpha\beta$-isonaph-

thaphenazine: these compounds may be represented by the general formula III.

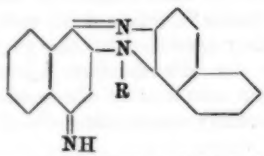


I. II. III.

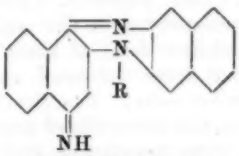
IV. *Naphthindulines*, or derivatives of naphthazine: as there are, theoretically, five possible naphthazines, of which, however, only three can yield indulines, the members of this group would be represented by the following three types:—



Symmetrical $\alpha\beta$-naphthinduline.



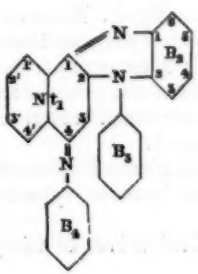
Asymmetrical $\alpha\beta$-naphthinduline.



$\alpha\beta$-$\beta\beta$-naphthinduline.

According to this system of nomenclature, the isoparatolylrosinduline previously described (1890, 908) would be termed paramethylphenylrosinduline, isonaphthylrosinduline (*loc. cit.*) would be symmetrical $\alpha\beta$-phenylnaphthinduline, and the so-called anilidoisonaphthylrosinduline (1891, 1044) would be symmetrical $\alpha\beta$-anilidophenylnaphthinduline.

It is also proposed that, for the purpose of referring to the position of groups in the several nuclei, the benzene rings should be distinguished by the signs B_1, B_2, B_3, &c., the nitrogen ring by the sign N_r,



and the naphthalene ring by the sign Nt, that nucleus containing the quinoneimide group being invariably referred to as B_1 or Nt_1; in addition, the benzene and naphthalene carbon atoms are numbered, those in combination with the two nitrogen atoms being invariably numbered 1 and 2 respectively.

"Amidoazobenzeneinduline," $C_{18}H_{13}N_3$ (Abstr., 1890, 764; 1891, 1046), melts at 215°, not at 135° as previously stated; it is formed in small quantity, together with an induline of the composition $C_{24}H_{18}N_4$, paraphenylenediamine, diparadiamidophenylamine, and complex dyes which are insoluble in water, when amidoazobenzene hydrochloride is boiled with aniline hydrochloride in aqueous solution.

B_2-4-*Anilidoinduline*, $NH{:}C_6H_3{<}\begin{matrix}N\\NPh\end{matrix}{>}C_6H_3{\cdot}NHPh$, is formed, together with a compound which has probably the composition $C_{30}H_{23}N_5$, when diphenylmetaphenylenediamine is treated with nitrosoaniline and concentrated hydrochloric acid in alcoholic solution; it forms well-defined crystals melting at 246°, and having a bronze lustre. It dissolves in concentrated sulphuric acid yielding a bluish-green solution, which turns blue and then violet on adding water. The *nitrate*, $C_{24}H_{18}N_4,HNO_3$, is a crystalline compound, soluble in hot water, with a reddish-violet coloration.

B_4-2-*Methylphenylrosinduline*, $C_{29}H_{21}N_3$, can be obtained by heating phenylrosinduline (Abstr., 1890, 908) with orthotoluidine; it crystallises in prisms or needles, having a bronze lustre, melts at 197°, and is decomposed into rosindone and orthotoluidine when heated at 170° with hydrochloric acid and acetic acid.

B_2-4-*Amidophenylrosinduline*, $C_{28}H_{20}N_4$, is formed when a mixture of Illinsky's nitroso-β-naphthylamine, aniline, and paraphenylenediamine hydrochloride is heated slowly to 150°, and kept at this temperature for one to two hours; it crystallises in lustrous, greenish-bronze-coloured plates, melts at 147° with decomposition, and dissolves in concentrated sulphuric acid, yielding a green solution which becomes reddish-violet on diluting; its salts are comparatively readily soluble in hot water. The constitution of this induline is proved by the facts that it is formed when anilidonaphthaquinoneanil is substituted for the nitroso-β-naphthylamine in the above-mentioned mixture, and that its diazo-derivative is converted into phenylrosinduline on treatment with boiling alcohol.

A *hydroxyrosinduline* of the composition $C_{22}H_{15}N_3O$ is obtained when the amidophenylrosinduline just described is heated with glacial acetic acid and concentrated hydrochloric acid at 190—200° for about eight hours; it crystallises in greenish, lustrous prisms, melts at about 270° with decomposition, and dissolves in alcohol, yielding an eosin-coloured solution, which shows a yellowish-red fluorescence; its solution in concentrated sulphuric acid is dirty green, but on adding water it turns brown, a red, flocculent substance being afterwards precipitated.

A *hydroxyrosindone* of the composition $C_{22}H_{14}N_2O_2$ is formed when amidophenylrosinduline or the hydroxyrosinduline just described is heated with hydrochloric acid and glacial acetic acid at 220—225° for 15—20 hours; it forms reddish-brown crystals, having a green lustre;

its solution in concentrated sulphuric acid is green, that in alkalis rose-red, and its alcoholic solution shows a brownish-green fluorescence.

The isorosindulines are most conveniently prepared by treating a nitroso-base, such as nitrosoaniline or nitrosodimethylaniline, with α-naphthylamine or with 2 : 2′-diphenylnaphthylenediamine in aniline solution.

B_1-*Dimethylisorosinduline hydrochloride*,

$$NMe_2Cl{\cdot}C_6H_3\!\ll\!\begin{matrix}N\\NPh\end{matrix}\!\gg\!C_{10}H_6,HCl,$$

can be obtained by heating nitrosodimethylaniline with aniline and α-naphthylamine hydrochloride, and subsequently converting the base into its hydrochloride. On treating the salt with soda, extracting with benzene, and evaporating the extract in absence of air, an *anhydride* of the base, having the composition $(C_{24}H_{20}N_3)_2O$, is deposited in almost black plates, which transmit red light; this compound decomposes at about 270°, rapidly absorbs carbonic anhydride from the air, and dissolves in concentrated sulphuric acid, yielding a green solution which changes, first, to dirty brown and then to reddish-violet on adding water. The *nitrate*, $C_{24}H_{19}N_3,2HNO_3$, crystallises in beautiful, green plates.

Nt_2-2′-*Anilido-αβ-isorosinduline*, $C_{28}H_{20}N_4$, is formed when 2 : 2′-diphenylnaphthylenediamine is warmed with nitrosoaniline and concentrated hydrochloric acid in alcoholic solution, and the hydrochloride thus produced decomposed with soda; it forms lustrous, bronze-coloured crystals, melts at a very high temperature, and dissolves in concentrated sulphuric acid, giving a yellowish-brown solution which, passing through green, becomes violet on diluting. The *hydrochloride*, $C_{28}H_{20}N_4,2HCl$, dissolves in alcohol with a violet, and in chloroform with a blue, coloration; the *platinochloride*, $C_{28}H_{20}N_4,H_2PtCl_6$, is a dark blue, crystalline compound.

Nt_2-2′-*Anilidophenyl-αβ-isorosinduline*, $C_{34}H_{24}N_4$, prepared from paranitrosodiphenylamine, dissolves in chloroform with a blue, and in concentrated sulphuric acid with a dirty violet, coloration. The *hydrochloride*, $C_{34}H_{24}N_4,HCl$, separates from alcohol in crystals; the *platinochloride*, $(C_{34}H_{24}N_4)_2,H_2PtCl_6$, forms lustrous, bronze-coloured crystals, and dissolves in alcohol with a blue coloration.

Nt_2-2′-*Hydroxyisorosindone*, $C_{22}H_{14}N_2O_2$, is formed when the preceding compound is heated with concentrated hydrochloric acid at 180°; it forms small, bronze-coloured, lustrous crystals, and dissolves in soda with a deep blue, in ammonia and concentrated sulphuric acid with a violet, coloration; its alcoholic solution is red, and shows a green fluorescence.

An *induline ammonium base* of the composition $C_{30}H_{24}N_4O$, is obtained when nitrosodimethylaniline is heated with diphenylnaphthylenediamine and concentrated hydrochloric acid in alcoholic solution and the product decomposed with soda; it separates from alcohol in lustrous, bronze-coloured crystals, and dissolves in concentrated sulphuric acid, yielding a green solution, which passes through reddish-violet and becomes blue on the addition of water. The *hydrochloride*, $C_{30}H_{22}N_4,2HCl$, separates from alcohol in crystals, and is moderately easily soluble in water.

Three naphthindulines, namely, symmetrical $\alpha\beta$-phenylnaphthinduline (see above), symmetrical $\alpha\beta$-anilidophenylnaphthinduline (naphthyl blue), and symmetrical Nt_2-4-anilidonaphthinduline (naphthyl violet), are formed when benzeneazo-α-naphthylamine hydrochloride (1 part) is heated with α-naphthylamine hydrochloride (1 part) and aniline (10 parts); when, however, the proportion of α-naphthylamine hydrochloride is diminished, symmetrical $\alpha\beta$-naphthinduline and other dyes are also obtained.

$\alpha\beta$-Naphthinduline, $C_{26}H_{17}N_3$, is a black, crystalline substance with a green lustre; it melts at 248—250°, and is insoluble in water: it dissolves in concentrated sulphuric acid, yielding a blue solution, which, on diluting with water, first becomes violet, then dirty green, and finally red. Its solutions in acetic acid and in dilute hydrochloric acid have a magenta colour, and the alcoholic and acetic acid solutions of its salts are characterised by their fiery red fluorescence. The *sulphate* crystallises in brownish-red, moss-like needles. When the base is heated with a mixture of glacial acetic acid and concentrated hydrochloric acid at 200°, it yields oxynaphthindone (oxyphenyldinaphthazine), identical with the compound melting at 295°, previously described (Abstr., 1890, 910).

Numerous naphthindulines are formed by the interaction of nitroso-β-naphthylamine, aniline, and α-naphthylamine, the character of the product depending on the conditions of the experiment; when the nitroso-compound (1 part) is heated with α-naphthylamine hydrochloride (2 parts) and aniline (10 parts) at 100°, naphthyl violet and naphthyl blue appear to be the only dyes formed.

Symmetrical *$\alpha\beta$-Nt_2-4-anilidonaphthinduline* (*naphthyl violet*), $C_{32}H_{22}N_4$, prepared by either of the methods mentioned above, crystallises in brown plates, having a bronze lustre, and melting at a very high temperature; it dissolves in alcohol, benzene, ether, and chloroform with a reddish-violet, in glacial acetic acid with a bluish-violet, coloration, and its salts, although very sparingly soluble in water, are readily soluble in alcohol, yielding bluish-violet dichroïc solutions, which transmit red, and reflect blue, light. It dissolves in concentrated sulphuric acid with a green coloration, but, on adding water to the solution, a blue, flocculent precipitate is produced; although solutions of its salts show only a feeble, brownish-red fluorescence, silk dyed with the solutions is highly fluorescent. The sulphonic acid is employed commercially and known as naphthyl violet. When the base is heated with glacial acetic acid at 200°, it is converted into an *anilidonaphthindone* of the composition $C_{32}H_{21}N_3O$; this compound crystallises in very dark, blue plates, which appear violet by transmitted light, and its solution in concentrated sulphuric acid is blue; it dissolves in alcohol with a reddish-violet coloration and a brownish-red fluorescence, but, on adding a mineral acid and diluting largely, the fluorescence changes to a bluish-green, the colour of the solution remaining unchanged. Nt_2-4-Anilidonaphthinduline is decomposed by a mixture of glacial acetic acid and concentrated hydrochloric acid at 200°, yielding Nt_2-4-oxynaphthindone, $C_{24}H_{14}N_2O$, identical with the compound previously obtained from symmetrical $\alpha\beta$-anilidophenylnaphthinduline (Abstr., 1891, 1044); this naphth-

indone crystallises in rectangular plates, and decomposes at about 300°.

Symmetrical $\alpha\beta$-anilidophenylnaphthinduline (naphthyl blue) is a phenyl derivative of naphthyl violet, the anilido-group probably occupying the Nt_2-4-position in both cases; its constitution is determined by the study of its products of decomposition with acids (Abstr., 1891, 1044) and by the fact that it can be formed by the condensation of benzeneazophenyl-α-naphthylamine (compare D.R.P. 63181). When the hydrochloride of the last-named compound is dissolved in phenol and the solution heated at 120—150°, ammonium chloride separates, and the solution turns violet; after treating with dilute soda to remove the phenol, and extracting the blue precipitate with alcohol and hydrochloric acid, the hydrochloride of symmetrical $\alpha\beta$-anilidophenylnaphthinduline remains in lustrous needles. The alkali salt of the sulphonic acid of this naphthinduline is a dark-brown, lustrous powder, and constitutes the naphthyl blue of commerce.

$\alpha\beta$-Anilidonaphthindone, $C_{32}H_{21}N_3O$, is formed, with separation of aniline, when $\alpha\beta$-anilidophenylnaphthinduline is heated with 50 per cent. acetic acid at 250°; it crystallises in bluish-black, lustrous plates, which appear violet by transmitted light, and dissolves in alcohol with a reddish-violet coloration, the solution showing a brownish-red fluorescence; it dissolves in concentrated sulphuric acid, yielding a blue solution, in which a red, flocculent precipitate is produced on the addition of water.

When the $\alpha\beta$-oxynaphthindone, obtained by decomposing $\alpha\beta$-anilidophenylnaphthinduline with a mixture of concentrated hydrochloric acid and glacial acetic acid, is heated with acetic anhydride and sodium acetate, it is converted into an *acetyl* derivative of the composition $C_{28}H_{18}N_2O_3$; this compound crystallises in slender, red, lustrous needles, melts at 290—295°, and dissolves in concentrated sulphuric acid with a reddish-violet coloration. The corresponding *benzoyl* derivative, $C_{33}H_{22}N_2O_3$, forms reddish-brown, lustrous crystals, and dissolves in concentrated sulphuric acid with a greenish-blue coloration. The *ethyl* derivative, $C_{28}H_{20}N_2O_2$, crystallises in lustrous, red plates or needles, and dissolves in alcohol, yielding a blood-red solution, which becomes orange and acquires a green fluorescence when acidified. The *methyl* derivative, $C_{27}H_{18}N_2O_2$, forms lustrous plates, melts above 330°, and dissolves freely in alcohol with a cherry-red coloration. The *bromo*-derivative, $C_{26}H_{12}N_2O_2Br_2$, prepared by treating the oxynaphthindone with a chloroform solution of bromine, crystallises in lustrous, reddish plates.

In preparing $\alpha\beta$-anilidophenylnaphthinduline from benzeneazo-α-naphthylamine, or from nitroso-β-naphthylamine, phenylrosinduline, anilidonaphthaquinonedianil (Abstr., 1891, 1044), and other substances are obtained as bye-products. Anilidonaphthaquinonedianil separates from a mixture of benzene and light petroleum in orange-yellow plates melting at 159°, and from alcohol in orange-red prisms, which melt at 142—143° and contain $\frac{1}{2}$ mol. C_2H_6O.

A substance, which appears to have the composition $C_{26}H_{17}N_3$, and which is, in all probability, an anilido-derivative of symmetrical $\alpha\beta$-naphthazine, is formed when nitroso-β-naphthylamine is treated

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with α-naphthylamine hydrochloride and aniline under particular conditions; it crystallises in yellowish-brown needles, having a greenish lustre, melts at 280°, and its solutions in alcohol and benzene show a green fluorescence; it dissolves in glacial acetic acid with a bluish-violet coloration. When this anilidonaphthazine is heated with glacial acetic acid and concentrated hydrochloric acid at 200°, it is decomposed into aniline and an *oxynaphthazine* of the composition $C_{20}H_{12}N_2O$; the latter crystallises in dark red needles, dissolves in concentrated sulphuric acid with a blue coloration, and forms a *hydrochloride* which crystallises in dark red needles having a green reflex; on distillation with zinc-dust, it yields symmetrical naphthazine.

When α-nitroso-β-naphthol is heated with α-naphthylamine hydrochloride and α-naphthylamine in alcoholic solution, hardly a trace of a naphthinduline is formed; if, after boiling for 6—7 hours, the solution be kept for a long time, a compound of the composition $C_{20}H_{20}N_2O$ is deposited in brown crystals. This substance melts at 237°, and dissolves in concentrated sulphuric acid, yielding a green solution, which turns blue on adding a little water, but becomes violet on diluting largely, a bronze-coloured powder being finally precipitated; it is probably a *naphthalidonaphthaquinonenaphthalide* of the constitution $\begin{matrix}C_6H_4\cdot C(N\cdot C_{10}H_7)\\ CO\cdot C(NH\cdot C_{10}H_7)\end{matrix}\!\!>\!\!CH$. The mother liquors from this product yield, on evaporation, a compound of the composition $C_{40}H_{27}N_3O$, which is probably a *dinaphthalidonaphthaquinoneanilide;* it crystallises in brownish-red plates, melts at 212°, and dissolves in concentrated sulphuric acid with a blue coloration, the solution becoming violet, then dirty red, and a red, flocculent substance separating, on the addition of water. F. S. K.

Isoparatolylrosinduline. By C. Schraube and E. Romig (*Ber.*, **26**, 575—582).—Having obtained an induline (azocarmine) by heating benzeneazo-α-naphthylamine hydrochloride with aniline and aniline hydrochloride (D.R.P., No. 45370), the authors attempted to prepare a homologue by similarly treating benzeneazoparatolyl-α-naphthylamine, but found that an induline, identical with that previously obtained, was produced. Fischer and Hepp having subsequently described an isoparatolylrosinduline, which they prepared by heating benzeneazoparatolyl-α-naphthylamine with aniline and alcohol (Abstr., 1890, 908), the authors have made a fresh investigation of the subject, in order to explain the difference in the results of the two series of experiments. They have synthesised isoparatolylrosinduline in the manner described below, and find that it has properties quite different from those assigned to it by Fischer and Hepp; the substance described by the latter was, without doubt, simply impure phenylrosinduline.

Chloronitrotoluenesulphonic acid [$Me : SO_3H : NO_2 : Cl = 1:2:4:5$] is obtained when metachlorotoluene is dissolved in ice-cold anhydrosulphuric acid, the solution warmed at 50° until a portion gives no precipitate on adding water, and, after cooling, treated with a mixture of concentrated sulphuric and nitric acids at 20—25°; it was isolated in the form of its *barium* salt, which crystallises in yellowish-brown plates or needles containing 2 mols. H_2O. When the barium salt is

reduced with zinc-dust in boiling aqueous solution, the chloramidotoluenesulphonic acid obtained in this way, boiled with moderately dilute sulphuric acid, and the diluted solution treated with soda, *chloramidotoluene* is precipitated; this base forms a colourless, crystalline hydrochloride, and, since it yields only a diazoamido-derivative with paranitrodiazobenzene, and not an amidoazo-derivative, it must be a chloroparatoluidine.

The *aniline* salt of *nitrotolylphenylaminesulphonic acid*

$$[Me : SO_3H : NO_2 : NHPh = 1 : 2 : 4 : 5]$$

is formed when the barium salt of chloronitrotoluenesulphonic acid is boiled with aniline hydrochloride in aqueous solution and the sparingly soluble aniline chloronitrotoluenesulphonate, which is precipitated in long, yellow needles, heated with aniline at 160° for 2—3 hours; the salt crystallises in brownish-yellow needles, and is only sparingly soluble in water. The corresponding *sodium* salt crystallises in golden plates. The *barium* salt crystallises in yellow plates with 2 mols. H_2O.

Nitrotolylphenylamine [Me : NHPh : NO_2 = 1 : 5 : 4] is produced when the barium salt just mentioned is treated with dilute sulphuric acid and the solution of the sulphonic acid heated with sulphuric acid at 145°; it crystallises in yellowish-red, six-sided plates, and melts at 110°.

Phenylorthotoluylenediamine, $NHPh\cdot C_6H_3Me\cdot NH_2$ [Me : NH_2 : NHPh = 1 : 4 : 5], prepared by reducing the preceding compound with zinc-dust in ammoniacal alcoholic solution, crystallises in slender, colourless needles, and melts at 87—88°.

Isoparatolylrosinduline, $C_6H_3Me<\begin{matrix}N=C\cdot C_6H_4\\ NPh\cdot C:CH\end{matrix}>C:NPh$, is produced when phenylorthotoluylenediamine (110 parts) and β-hydroxy-α-naphthaquinoneanil (130 parts) are boiled with a mixture of 37 per cent. hydrochloric acid (50 parts) and alcohol (1000 parts) until solution is complete and the deep-red colour ceases to become more intense; on adding ammonia to the hot solution, isoparatolylrosinduline is precipitated in slender, brownish-red needles melting at 224·5°. It separates from hot alcoholic benzene in dark-brown, lustrous crystals, which appear red by transmitted light; it dissolves in concentrated sulphuric acid with a green coloration.

F. S. K.

Acetalylphenylcarbamide. By P. Fritsch (*Ber.*, **26**, 427—428). —This substance, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, is obtained by treating acetalamine with phenylic cyanate; it forms long needles with a silky lustre, and melts at 55°. When warmed with dilute sulphuric acid (1 : 2), it is converted into a substance $CO<\begin{matrix}NPh\cdot CH\\ NH-CH\end{matrix}>$, which forms a white, crumbly mass, melts above the boiling point of sulphuric acid, and, when treated with sodium methoxide and methylic iodide, yields a *methyl derivative* which melts at 216°, and forms small, silky crystals.

C. F. B.

Constitution of Thiocarbamide and Phenyldithiobiuret. By A. CLAUS (*J. pr. Chem.* [2], **47**, 135—138).—A discussion of the subject designed to show that it is incorrect to argue that a sulphur compound is a thioalcohol or thiophenol, because it is convertible into a thio-ether by the action of an alkyl haloïd and an alkali. This has a special bearing on Fromm's interpretation of the reactions of phenyldithiobiuret (Abstr., 1892, 844), which, in the author's opinion, by no means prove the existence of two SH groups in that compound. A. G. B.

Action of Diazobenzene Chloride on α-Hydroxyuvitic acid. By A. BLANK (*Ber.*, **26**, 602—604).—It is stated in a recent French patent (No. 221,370) that α-hydroxyuvitic acid reacts readily with diazo-compounds, yielding products in which the azo-group occupies the meta-position relatively to the hydroxy-radicle; such a result being contrary to all experience, the author has investigated the matter, and found the statement to be incorrect.

When an ice-cold solution of α-hydroxyuvitic acid in 15 per cent. sodium carbonate is treated with diazobenzene chloride, a yellow, crystalline sodium salt is formed. The acid obtained on decomposing this sodium salt with hydrochloric acid crystallises in lustrous, yellow plates, melts at 198—199° (uncorr.), and decomposes at a higher temperature with evolution of carbonic anhydride; it is identical with the compound obtained by the action of diazobenzene chloride on orthohydroxymetatoluic acid, so that it must be a benzeneazoorthohydroxymetatoluic acid of the constitution $N_2Ph\cdot C_6H_2Me(OH)\cdot COOH$ [$N_2Ph : Me : OH : COOH = 1 : 3 : 4 : 5$]. F. S. K.

Dihydrobenzaldehyde. By A. EINHORN (*Ber.*, **26**, 451—458).—In the light of the constitutional formula for anhydroecgonine, recently proposed by Einhorn and Tahara (this vol., i, 377), the author now considers that the dihydrobenzaldehyde obtained from this compound (Abstr., 1891, 65) is the $\Delta^{4:6}$-derivative, and the following experiments support this hypothesis.

Dihydrobenzamide, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CH-CH\\CH_2\cdot CH_2\end{matrix}\begin{matrix}>\\<\end{matrix}C\cdot CONH_2$, is obtained by treating the dihydrobenzoic acid (*loc. cit.*) with phosphoric chloride, and pouring the solution into concentrated aqueous ammonia. It crystallises from ether in white needles, and melts at 105°.

When a 12 per cent. solution of bromine in chloroform is added to one of dihydrobenzoic acid in the same solvent, a *dibromo*-additive product is formed; it crystallises from alcohol in white, prismatic tables, and melts at 166°. A *tetrabromide* is obtained when the dihydrobenzoic acid is dissolved in glacial acetic acid and heated with bromine in a sealed tube at 100°; it crystallises from benzene in nodular groups of crystals, and melts at 183°. On heating the dihydrobenzoic acid with sodium amalgam and water, it is converted into Δ^1-tetrahydrobenzoic acid (Aschan, this vol., i, 34).

A. R. L.

α-Phenylcinnamic acid. By R. MÜLLER (*Ber.*, **26**, 659—665).—α-Phenylcinnamic acid is purified by crystallisation from light petr-

oleum, and melts at 172°, instead of 169—170° as stated by Oglialoro; attempts to isolate a second modification by fractional crystallisation of the sodium and barium salts were unsuccessful. The acid does not combine directly with bromine, but yields an additive compound by the action of hydrogen bromide at 125°; this is deposited from alcohol in needles, melts at 185°, and on treatment with alcoholic potash yields stilbene.

Methylic α-phenyldibromocinnamate, which melts at 111° instead of 106—108°, as stated by Cabella, gives *methylic α-phenyl-β-bromocinnamate* by the action of alcoholic potash; this crystallises from dilute alcohol in groups of colourless needles, melts at 70°, and on hydrolysis yields α-phenylcinnamic acid; on reduction of the bromo-salt in acid solution, methylic phenylcinnamate is regenerated.

Bromostilbene is formed in small quantity in the preparation of methylic α-phenyl-β-bromocinnamate, and is readily obtained by the action of bromine on sodium α-phenylcinnamate in molecular proportion in aqueous solution at 40—45°; it crystallises in prisms, and melts at 22—25°. J. B. T.

Phenyl-α-hydroxycrotonic acid. By G. PULVERMACHER (*Ber.*, **26**, 462—464).—The compound, melting at 98°, which Biedermann obtained from phenyl-α-hydroxycrotonic acid and phenylhydrazine (Abstr., 1892, 473), has probably the constitution $NPh<\begin{matrix}CO\\NH\end{matrix}>CH\cdot CH{:}CHPh$. When it is boiled with hydriodic acid and phosphorus, it yields phenyl-α-hydroxycrotonic acid, ammonia, and aniline. A certain amount of phenylhydrazine is obtained when the compound is boiled with alkalis, or fuming hydrochloric acid; also when it is treated with cold fuming hydrobromic acid. γ-Phenylbutyric acid is formed by heating the compound with hydriodic acid and phosphorus at 160° in a sealed tube. A. R. L.

Bergapten. By C. POMERANZ (*Monatsh.*, **14**, 28—32; compare Abstr., 1892, 71).—In continuation of his investigation of this substance, the author has obtained *nitrobergapten*, $C_{12}H_7(NO_2)O_4$, by the action of nitric acid on bergapten moistened with acetic acid; it crystallises from the latter in pale yellow needles, becomes brown at 230°, and melts at 256° with decomposition. When triturated with a little acetic acid, and allowed to remain for an hour with 20 times its weight of fuming nitric acid, it yields a product which, in addition to unaltered nitrobergapten, contains *nitromethoxycumaronecarboxylic acid*, $CH<\begin{matrix}CH\\O\end{matrix}>C_6(OH)(OMe)(NO_2)\cdot COOH$, and the corresponding *aldehyde*. The former crystallises in pale yellow, prismatic needles, and melts at 200° with decomposition, and the latter forms small, yellowish-red crystals, which darken at 200°, and decompose at a higher temperature. These results are in full agreement with the views already expressed as to the constitution of bergapten, and the author is now endeavouring to ascertain the exact orientation of the different groups in the benzene nucleus. H. G. C.

Chestnut Bark Tannin. By H. Trimble (*Chem. News*, **67**, 7, 8).—With the object of comparing the tannin from chestnut bark with that from the wood, material was taken from a tree 30 years old, cut in August, and from which the bark was immediately removed, air-dried, and powdered. The total tannin was found to be 7·31 per cent., the wood yielding 7·85 per cent.; the bark also contained resin 1·09, mucilage 3·06, glucose 1·35, moisture 10·0, ash 4·71, and cellulose 45·44 per cent. The tannin, as extracted from the bark by commercial ether, was darker than that from the wood; but nevertheless, after systematic purification, in a manner somewhat similar to that already described (Abstr., 1892, 716), it proved to be identical with the chestnut wood tannin. D. A. L.

Derivatives of Gallic acid. By A. Biétrix (*Bull. Soc. Chim.* [3], **7**, 623—625).—*Ethylic dibromogallate*, $C_6Br_2(OH)_3{\cdot}COOEt$, obtained by treating ethylic gallate with an excess of bromine, crystallises from water in delicate, translucent needles, and melts at 137°.

Methylic gallate, $C_6H_2(OH)_3{\cdot}COOMe$, is prepared by saturating a solution of gallic acid in methyl alcohol with hydrogen chloride; it crystallises from water in transparent needles containing 3 mols. H_2O, melts at 112°, and gives a blackish-green coloration with ferric chloride. The *dibromo*-derivative forms silky needles, and melts at 139°. A. R. L.

Parethoxyorthotoluenesulphonic acid and its Derivatives. By P. J. Dashiell (*Amer. Chem. J.*, **15**, 126—129).—In this paper *barium parethoxyorthotoluenesulphonate*, with 4 mols. H_2O, and the *lead*, with 3 mols. H_2O, *calcium*, with 3 mols. H_2O, *magnesium*, with 6 mols. H_2O, *zinc*, with 6 mols. H_2O, *copper*, with 6 mols. H_2O, *silver*, *potassium*, with 1 mol. H_2O, *sodium*, and *ammonium* salts are described. They were obtained from the acid prepared by the decomposition of paradiazotolueneorthosulphonic acid by alcohol (this vol., i, 325). The *sulphonic chloride* is a light brown, mobile oil. A. G. B.

Ethereal Sulphinates. By R. Otto and A. Rössing (*J. pr. Chem.* [2], **47**, 152—172).—Methylic β-naphthalenesulphinate has been already described (Abstr., 1892, 623). The compound which is simultaneously produced during the preparation is β-naphthyl disulphoxide (m. p. 107°), not methylnaphthylsulphone formate, as previously suggested (*loc. cit.*). The sulphinate is easily oxidised to methylic β-naphthylsulphonate, which melts at 55—56° (Krafft and Roos, Abstr., 1892, 1219).

Methylic α-naphthalenesulphinate is prepared similarly to the β-derivative. It is a yellowish oil, has a slight odour, and dissolves easily in ether or alcohol, but only sparingly in boiling light petroleum. It is easily hydrolysed by potash, and is thus distinguished from its isomeride, methyl-α-naphthylsulphone (m. p. 102—103°). It is easily oxidised to methylic α-naphthylsulphonate, which melts at 78°, not 75° (Krafft and Roos, *loc. cit.*). Some α-naphthyldisulphoxide is produced during the preparation of the sulphinate, and is separated by light petroleum, in which which it is insoluble.

Ethylic β-naphthalenesulphinate, prepared from sodium β-naphthalenesulphinate and ethylic chlorocarbonate, is an aromatic, yellowish oil, insoluble in water, easily soluble in alcohol and ether, but only sparingly in light petroleum; it is readily hydrolysed by potash, and oxidised by potassium permanganate to the corresponding sulphonate.

Methylic benzenesulphinate, prepared from sodium benzenesulphinate and methylic chlorocarbonate, is a mobile oil, insoluble in water, but soluble in alcohol and ether. Hot water decomposes it into methyl alcohol and benzenesulphinic acid, which becomes converted into benzene disulphoxide and benzenesulphonic acid.

Methylic paratoluenesulphinate is a yellow oil which is very unstable in air. Oxidation converts it into the corresponding sulphonate, which melts at about 30°. With water, it behaves like the benzenesulphinate.

Methylic parabromobenzenesulphinate, from *sodium parabromobenzenesulphinate* (prepared from parabromobenzenesulphonic chloride and zinc-dust in alcohol) and methylic chlorocarbonate in methyl alcohol, is a yellowish oil, insoluble in water, but soluble in ether and alcohol.

Experiments with sulphinates other than those of the alkali metals showed that the reaction with alkyl chlorocarbonates always yields alkylic sulphinates. It was also proved that both zinc and silver sulphinates give sulphones when treated with alkylic haloïds, showing that there is no difference between their behaviour and that of the alkali sulphinates in this respect (Abstr., 1880, 810). Attempts to convert ethylic benzenesulphinate into its isomeric sulphone proved futile. A. G. B.

Chemical Behaviour of Ethereal Salts of Sulphinic acids. By R. Otto and G. Zuschlag (*Ber.*, **26**, 430—435).—A continuation of Otto and Rössing's experiments (preceding abstract). When a current of dry hydrogen sulphide is passed through ethylic benzenesulphinate heated at 110°, ethyl alcohol distils over, and when this ceases, the residue consists of phenylic benzenethiosulphonate; if, however, the current of gas be continued for a longer period, the residue consists of sulphur and a mixture of sulphur compounds similar to that obtained by Otto (*J. pr. Chem.* [2], **37**, 207) by the action of hydrogen sulphide on alcoholic solutions of benzenesulphinic acid. Ethylenediphenylsulphone undergoes no change when treated with hydrogen sulphide. When ethylic benzenesulphinate is shaken with an excess of a concentrated, colourless, aqueous solution of potassium sulphide, heat is developed. The oily portion of the product consists of a mixture of phenylic bisulphide (m. p. 60°) and liquids containing more sulphur, whilst the aqueous liquid contains alcohol and potassium benzenethiosulphonate; it yields, on treatment with carbonic anhydride, an oil. When the latter is distilled in a current of steam, thiophenyl passes over, and a mixture of sulphur, phenyl bisulphide, and higher sulphur derivatives remains. A. R. L.

Conversion of Pentene Derivatives into Indene Derivatives. By T. Zincke and H. Günther (*Annalen*, **272**, 243—270).—*Hexa-*

chloroketoindene, $C_6Cl_4<\begin{matrix}CO\\CCl\end{matrix}>CCl$, is formed when either of the hexachlorhydroxypentenecarboxylic acids previously described (Abstr., 1890, 754) is heated with 8—10 parts of water: the acid dissolves at first, but the solution quickly becomes turbid, carbonic anhydride is evolved, and the product is precipitated in a flocculent condition. The decomposition of the acid takes place in accordance with the equation $2C_6Cl_6H_2O_3 + H_2O = C_9Cl_6O + 6HCl + 3CO_2$, the yield of hexachloroketoindene being almost theoretical; attempts to isolate some intermediate product in order to throw light on this remarkable reaction were unsuccessful.

Hexachloroketoindene crystallises in golden plates, melts at 148—149°, and separates unchanged from nitric acid of sp. gr. 1·4; molecular weight determinations by the boiling point method confirm the molecular formula C_9Cl_6O. Its *oxime* melts at 255° with decomposition.

Pentachlor-α-anilido-α-ketoindene, $C_6Cl_4<\begin{matrix}CO\\C(NHPh)\end{matrix}>CCl$, prepared by heating the preceding compound with aniline in alcoholic solution, crystallises in lustrous, dark red needles, and melts at 236—237°; it is very stable towards alkalis, but is readily decomposed by acids. The corresponding *paratoluido-derivative*, $C_9Cl_5O\cdot NH\cdot C_7H_7$, obtained in like manner, melts at 243°.

Pentachlor-α-hydroxy-α-ketoindene, $C_6H_4<\begin{matrix}CO\\C(OH)\end{matrix}>CCl$, is formed when hexachloroketoindene is heated with alkalis, and also when the anilido-derivative just described is warmed with concentrated sulphuric acid for several hours. It is an orange, crystalline powder, melts at 177°, decomposes carbonates and alkali acetates, and readily changes into an insoluble, probably polymeric, modification; it separates from acetic acid in orange-red, and from benzene in colourless, crystals, which contain the solvent and are unstable. The *hydrate*, $C_9HCl_5O_2 + H_2O$, is obtained as a salmon-coloured precipitate on decomposing the sodium derivative with hydrochloric acid; it turns orange and begins to lose water at about 111° and melts at 174—177°. The *sodium* derivative crystallises in red needles, and seems to have the composition $C_9H_4Cl_5O_2Na$. A red, crystalline substance of the composition $C_{15}Cl_5H_8NO_2$ is formed when the hydroxy-compound is treated with aniline in glacial acetic acid solution; it melts at 205° and is readily decomposed by mineral acids. The *methoxide*, $C_{10}H_5Cl_5O_3$, prepared by boiling the hydroxy-compound or its hydrate, with methyl alcohol, crystallises in long, reddish-yellow needles, begins to lose methyl alcohol at 110°, and has no definite melting point; the corresponding *ethoxide* crystallises in yellow needles and is less stable. The *acetyl* derivative, $C_{11}H_3Cl_5O_3$, crystallises in lustrous, golden needles or plates, and melts at 178—179°.

Hexachlor-α-diketohydrindene, $C_6Cl_4<\begin{matrix}CO\\CO\end{matrix}>CCl_2$, prepared by treating pentachlorhydroxyketoindene with chlorine in glacial acetic acid solution, crystallises in short prisms, and melts at 155—156°.

Hexachloracetophenoneorthocarboxylic acid, $CHCl_2\cdot CO\cdot C_6Cl_4\cdot COOH$,

is formed when the diketone just described is treated with concentrated alcoholic potash in the cold; it crystallises in colourless needles, melts at 192—193°, previously softening, and forms a colourless, crystalline, insoluble silver salt.

Heptachloracetophenoneorthocarboxylic acid, $CCl_3{\cdot}CO{\cdot}C_6Cl_4{\cdot}COOH$, is deposited when the preceding compound is dissolved in excess of sodium carbonate, and chlorine passed into the solution; it is a colourless, crystalline substance, melts at 240—241°, and is decomposed by soda into chloroform and tetrachlorophthalic acid.

Octochlor-α-ketohydrindene, $C_6Cl_4<\begin{matrix}CO-\\CCl_2\end{matrix}>CCl_2$, is best prepared by heating hexachloroketoindene with manganese dioxide and hydrochloric acid at 180°; it forms colourless nodules, melts at 112—113°, and is reconverted into hexachloroketoindene on treatment with stannous chloride.

Hexachlorodibrom-α-ketohydrindene, $C_6Cl_4<\begin{matrix}CO\ \ -\\CClBr\end{matrix}>CClBr$, obtained by treating the hexachloro-compound with bromine, is an almost colourless, crystalline, granular substance, and melts at 105—106° with elimination of bromine, being reconverted into the hexachloro-compound.

Octochlororthovinylbenzoic acid, $CCl_2{:}CCl{\cdot}C_6Cl_4{\cdot}COOH$, is produced when octochloroketohydrindene is treated with alcoholic soda; it crystallises in lustrous, colourless needles, and melts at 158—159°; its *methylic* salt, $C_{10}H_3Cl_7O_2$, is a colourless, crystalline substance melting at 77—78°.

Octochlorindene, $C_6Cl_4<\begin{matrix}CCl_2\\CCl\end{matrix}>CCl$, prepared by treating hexachloroketoindene with phosphorus pentachloride at 190—200°, crystallises in colourless needles, and melts at 85°. F. S. K.

Derivatives of Phthalazine and Isoindole. By S. Gabriel and A. Neumann (*Ber.*, **26**, 521—527 and 705—713).—Phthalazone, $C_6H_4<\begin{matrix}CH\\CO\end{matrix}>N_2H$, is obtained by heating the product of the action of bromine on phthalide with water, neutralising the mixture of hydrobromic and phthaldehydic acids thus obtained with soda and then adding hydrazine sulphate to the hot solution. It crystallises in long, lustrous needles, melts at 182°, boils at 337° under 755 mm. pressure, and dissolves in alkalis and mineral acids. When reduced with zinc and hydrochloric acid, it is converted into phthalimidine.

3-*Methylphthalazone*, $C_6H_4<\begin{matrix}CH\\CO\end{matrix}>N_2Me$, is obtained by heating an alcoholic solution of phthalazone with soda and methylic iodide. It distils as a yellow oil at 301° under 755 mm. pressure, crystallises from acetic acid in forms resembling calc-spar, melts at 102—103°, and has basic properties.

4-*Chlorophthalazine*, $C_6H_4<\begin{matrix}CH\\CCl\end{matrix}>N_2$, is obtained by heating phthalazone with phosphorus oxychloride. It crystallises in yellow needles, melts at 113°, and dissolves easily in dilute acids. The solution of

the hydrochloride yields with gold chloride sparingly soluble, yellow needles, with potassium dichromate orange-yellow tablets, with picric acid slender needles, and with potassium ferrocyanide a brownish-yellow, crystalline powder. The *platinochloride*, $(C_8H_5N_2Cl)_2,H_2PtCl_6$, is sparingly soluble and crystallises in slender needles.

4-*Methoxyphthalazine*, $C_6H_4<\overset{\text{——}CH}{C(OMe)}>N_2$, is obtained by boiling amethyl alcoholic solution of chlorophthalazine with sodium methoxide. It crystallises in yellow needles, melts at 60—61°, has a faint, fruity odour, and yields crystalline salts.

Dihydroisoïndole, $C_6H_4<\overset{CH_2}{CH_2}>NH$, obtained by reducing chlorophthalazine with zinc and hydrochloric acid, is an oil which boils at 213° under 762 mm. pressure, and has an odour resembling that of benzylamine; it has an alkaline reaction, and takes up carbonic anhydride on exposure to the air to form a crystalline mass. The *hydrochloride* darkens and melts at 255—256°. The *platinochloride*, $(C_8H_9N)_2,H_2PtCl_6$, crystallises in flat, orange-yellow needles. The *nitrosamine*, $C_8H_8N\cdot NO$, crystallises in long, slender needles, and melts at 96—97°.

1-*Methylphthalazone*, $C_6H_4<\overset{CMe}{CO}>N_2H$, is obtained by adding a solution of hydrazine sulphate in sodium hydroxide to a solution of acetophenoneorthocarboxylic acid and heating the mixture for one hour on the water bath. It crystallises in short prisms, melts at 222°, boils at 347—348° under 755 mm. pressure, and is soluble in alkalis and acids.

1-*Methylphthalimidine*, $C_6H_4<\overset{CHMe}{CO}>NH$, or $C_6H_4<\overset{CHMe}{C(NH)}>O$, is obtained by reducing the preceding compound with zinc and hydrochloric acid. It distils at a very high temperature, crystallises in colourless, transparent rhombs, melts at 110—111°, is a feeble base, and yields a crystalline aurochloride and platinochloride.

1 : 3-*Methylethylphthalazone*, $C_6H_4<\overset{CMe}{CO}>N_2Et$, is obtained by boiling an alcoholic solution of methylphthalazone with sodium hydroxide and ethylic iodide. It boils at 309° under 735 mm. pressure, melts at 75—76°, and is soluble in hydrochloric acid.

The hydrazone ethiodide of acetophenonecarboxylic acid,

$$COOH\cdot C_6H_4\cdot CMe{:}N_2H_2EtI,$$

is obtained as sodium salt in the preparation of the preceding compound. It crystallises in thick, colourless prisms, and melts at 188—189° with formation of water, ethylic iodide, and 1-methylphthalazone. It is a strong acid, dissolving easily in ammonia and the fixed alkalis, and turns out carbonic anhydride from carbonates; it is precipitated from these solutions in a crystalline condition by strong acids.

The bye-product obtained in methylating phthalazine is very similar to the last compound, and is the *hydrazone methiodide of phthalaldehydic acid*, $COOH\cdot C_6H_4\cdot CH{:}N_2H_2MeI$. It melts at 179—180°

with decomposition into phthalazone, and is precipitated from its salts by hydrochloric acid in lustrous rhombs or needles.

1 : 4-*Methylchlorophthalazine*, $C_6H_4<\begin{matrix}CMe\\CCl\end{matrix}>N_2$, obtained by the action of phosphorus oxychloride on 1-methylphthalazone, crystallises in long, lustrous needles, melts at 130°, has basic properties, and yields crystalline salts.

1 : 4-*Methylethoxyphthalazine*, $C_6H_4<\begin{matrix}-CMe\\C(OEt)\end{matrix}>N_2$, is obtained by boiling the preceding compound with sodium ethoxide and alcohol. It crystallises in slender needles, melts at 56—57° and is easily soluble in acids. The solution in hydrochloric acid gives crystalline precipitates with picric acid, potassium dichromate, platinic chloride, and potassium ferrocyanide.

Methylisoindole, $C_6H_4<\begin{matrix}CMe\\CH_2\end{matrix}>N$ or $C_6H_4<\begin{matrix}CHMe\\-CH\end{matrix}>N$, is obtained by reducing methylchlorophthalazine with hydriodic acid and phosphorus, or better with zinc and hydrochloric acid, when it is obtained as the *zinc double salt*, $(C_9H_9N)_2,H_2ZnCl_4$. The *platinochloride*, $(C_9H_9N)_2,H_2PtCl_6,H_2O$, crystallises in slender, yellow needles, does not lose its water of crystallisation at 100°, and decomposes at a higher temperature. The *picrate*, $C_9H_9N,C_6H_3N_3O_7$, is obtained as a fine crystalline precipitate. The *free base* is a colourless oil with an odour resembling that of quinoline; it is volatile with steam and quickly turns yellow on exposure to air. A wood splinter remains uncoloured when placed in an acid solution of the base, but if alkali is added and the mixture boiled, a cherry-red coloration is produced.

1-*Methyldihydroisoindole*, $C_6H_4<\begin{matrix}CHMe\\CH_2-\end{matrix}>NH$, is obtained by the further reduction of methylchlorophthalazine with zinc and hydrochloric acid. It distils at 213° under 758 mm. pressure, has a strong alkaline reaction when dissolved in water, and absorbs carbonic anhydride. The *hydrochloride* crystallises in very slender needles, and melts at 170° with a violet coloration. The *nitrosamine* crystallises in lustrous spears, and melts at 98°.

1-*Benzylphthalazone*, $C_6H_4<\begin{matrix}C(CH_2Ph)\\CO-\end{matrix}>N_2H$, is obtained by the action of hydrazine sulphate on an alkaline solution of desoxybenzoïncarboxylic acid. It crystallises in long, colourless needles, and melts at 196°. When treated with phosphorus oxychloride, it yields 1 : 4-benzylchlorophthalazine; this crystallises in long, lustrous needles, and melts at 152°. E. C. R.

Indigotintrisulphonic and Indigotintetrasulphonic acids. By P. Juillard (*Bull. Soc. Chim.* [3], **7**, 619—621).—Indigotin dissolves in 30 per cent. anhydrosulphuric acid (25 parts) with a characteristic reddish-brown colour; when the product is cautiously poured into ice-cold water, and sodium chloride added to the solution, a red-brown *salt*, $C_{16}H_8N_2O_2(SO_3Na)_4 + 10H_2O$, separates. Its aqueous solution gives a blue precipitate on the addition of barium chloride, which, when decomposed with sulphuric acid, yields a mixture of indigotintrisulphonic and

tetrasulphonic acids. In aqueous solution, the acids dye wool and silk a bluish-red shade. A. R. L.

Carbazole. By A. Mazzara and E. Leonardi (*Gazzetta*, **22**, ii, 569—582.—*Benzoylbromocarbazole*, $NBz<^{C_6H_4}_{C_6H_3Br}$, is obtained by brominating benzoylcarbazole in acetic acid solution. It forms small, transparent crystals, melts at 124—125° (corr.), and is very soluble in chloroform, toluene, carbon bisulphide, or benzene, but dissolves less readily in glacial acetic acid or light petroleum. On treatment with alcoholic potash, it yields the bromocarbazole, melting at 199°. On brominating carbazole, or its acetyl or benzoyl derivatives, in acetic acid solution at 100—115°, the corresponding bromo-derivative and a quantity of resinous matter are obtained, together with a *substance* having the composition $C_{12}H_8NBr,C_{12}H_9N$, which forms transparent, colourless scales, melting at 193—195°. This, however, behaves towards acetic anhydride and picric acid as a mere mixture of carbazole and bromocarbazole.

Benzoyldibromocarbazole, $NBz<^{C_6H_3Br}_{C_6H_3Br}$, prepared in a manner similar to the mono-derivative, forms transparent needles or prisms melting at 215—216° (corr.); it is soluble in chloroform or toluene, but only sparingly so in alcohol or light petroleum. On treatment with alcoholic potash, it yields *dibromocarbazole*, $NH<^{C_6H_3Br}_{C_6H_3Br}$; this substance forms small, colourless prisms, melting at 212—213° (corr.).

Benzoylnitrobromocarbazole, $NBz<^{C_6H_3\cdot NO_2}_{C_6H_3Br}$, prepared by nitrating benzoylbromocarbazole, forms minute, translucent, yellow needles, melting at 267—268° (corr); it is sparingly soluble in chloroform, toluene, carbon bisulphide, alcohol, or light petroleum, and is accompanied by a small quantity of another substance melting above 200°.

Nitrobromocarbazole, $NH<^{C_6H_3\cdot NO_2}_{C_6H_3Br}$, is obtained by boiling its benzoyl derivative with alcoholic potash. It forms small, hard, yellow needles, which begin to sublime at 225°, and melt at 288—289° (corr.); it is soluble in acetic acid or benzene, sparingly so in alcohol or ether. Its *acetyl* derivative, $NAc{\cdot}C_{12}H_6Br{\cdot}NO_2$, forms small, whitish crystals, which rapidly turn yellow on exposure to light, and melt at 236—237° (corr.); it is soluble in benzene, but only sparingly so in alcohol or light petroleum.

Benzoylnitrobromocarbazole, identical with that described above, is obtained by brominating benzoylnitrocarbazole; the nitrobromocarbazole derived from the former substance would seem to contain both the bromine and the nitro-group in the para-position relatively to the imidogen group. From a consideration of the work of Blank (Abstr., 1891, 571), it is very probable that the nitrocarbazole pre-

pared by the authors (Abstr., 1892. 616) also contains the imidogen and nitro-groups in the para-position relatively to each other.

W. J. P.

A New Acridine and an Acridylpropionic acid. By A. VOLPI (*Gazzetta*, **22**, ii, 549—556).—An *acridine*, $C_{30}H_{43}N$, is formed on heating a mixture of stearic acid, diphenylamine, and zinc chloride at 220°, and is purified by means of its hydrochloride; the free base separates from dilute alcohol in long, thin, yellow needles or crystalline laminæ melting at 69—70°. It is soluble in all ordinary solvents, with the exception of water; its dilute solutions have a blue fluorescence, whilst solutions of its salts show a green fluorescence. Contact with acid vapours rapidly turns it yellow, and light also changes it. The *hydrochloride*, $C_{30}H_{43}N,HCl$, forms minute needles, and is soluble in alcohol or benzene. The *platinochloride*,

$$(C_{30}H_{43}N)_2,H_2PtCl_6,$$

is obtained in yellow crystals melting at 190°. The sulphate, $C_{30}H_{43}N,H_2SO_4$, is soluble in alcohol or benzene, and melts at 149°; all the salts are decomposed by water. The differences observed between this substance and pentadecylacridine (Abstr., 1892, 342) are very slight, and the author is comparing the two bases, in order to determine whether they are identical.

Acridylpropionic acid, $C_{13}H_8N\cdot C_2H_4\cdot COOH$, is obtained on heating a mixture of succinic acid, diphenylamine, and zinc chloride at 180—205°, and is purified by recrystallising its sodium salt, which is then decomposed by passing carbonic anhydride through its aqueous solution. The acid forms a yellow, crystalline powder, which does not melt at 300°, is insoluble in water, benzene, ether, or chloroform, and almost insoluble in hot alcohol. It dissolves in dilute acids or alkalis; the acid solutions have a green, whilst the alkaline solutions show a blue, fluorescence. The *sodium* salt, $NaC_{16}H_{12}NO_3,2\frac{1}{2}H_2O$, loses its water at 100°, is very soluble in water, and is insoluble in ether or benzene; it decomposes at 260° without melting. Its aqueous solution gives yellow precipitates with mercuric, mercurous, or silver salts, or picric acid; a green precipitate is obtained with copper sulphate. The *silver* salt forms yellow flocks. The *hydrochloride*, $C_{16}H_{13}NO_2,HCl$, forms fairly large crystals, which melt at 268° with previous decomposition. The *platinochloride* probably contains 1 mol. H_2O, which it loses at 115—120°; it forms microscopic, yellow crystals, decomposing at 259°.

W. J. P.

Formation of Stilbene. By A. KLAGES and E. KNOEVENAGEL (*Ber.*, **26**, 447—451).—When deoxybenzoïn is dissolved in a molecular proportion of benzaldehyde, and the solution saturated with hydrogen chloride, chlorobenzyldeoxybenzoïn, $COPh\cdot CHPh\cdot CHPhCl$, is formed; it crystallises from glacial acetic acid in small needles, melts at 180—182°, and a small quantity of a compound (perhaps a stereoisomeride) melting at 153° can be isolated from the mother liquor. When either of these compounds is heated, benzoic chloride and stilbene pass over. By the action of dilute alkali on chlorobenzyldeoxybenzoïn, benzamarone is obtained; whilst by adding the com-

pound to hot concentrated aqueous potash, benzylidenedeoxybenzoïn is formed. *Benzylidenedeoxybenzoïn dibromide* crystallises in nacreous leaflets or needles, and melts at 135°. *Iodobenzyldeoxybenzoïn* is prepared from deoxybenzoïn, benzaldehyde, and hydriodic acid. It melts between 155° and 170°, according to the solvent from which it is crystallised, and is probably a mixture of stereoisomerides.

A. R. L.

Condensation of Orthochlorobenzal Chloride by means of Metals. By A. H. Gill (*Ber.*, **26**, 649—652).—Orthochlorotoluene is prepared from orthotoluidine by means of the diazo-reaction; the yield is 40 per cent. of the theoretical. On treatment with chlorine at about 160°, orthochlorobenzal chloride is obtained; this boils at 228·5°; its sp. gr. = 1·399 at 15°; it is not acted on by sodium at 160°, and only undergoes slight change with zinc dust or finely divided copper at 100—110°. On heating the chloride with methyl alcohol and a mixture of equal parts of sand and finely divided silver for six hours at 95°, *orthodichlorostilbene dichloride*,

$$C_6H_4Cl\cdot CHCl\cdot CHCl\cdot C_6H_4Cl,$$

is formed, and on the addition of light petroleum to its ethereal solution, is deposited in rhombic crystals melting at 170·5°. The yield is 8 per cent. of the benzal chloride employed.

Orthodichlorostilbene, $C_6H_4Cl\cdot CH{:}CH\cdot C_6H_4Cl$, is prepared by heating the preceding compound with finely divided copper at 100—105°, or by the action of a mixture of sand and copper on orthochlorobenzal chloride; in this case the yield is 12 per cent. of the chloride employed; the compound boils at about 220°, and is deposited from alcohol in long, colourless needles, and from toluene in rhombic prisms, which melt at 97°. Attempts to eliminate the remaining chlorine atoms were unsuccessful. By the action of chlorine, the dichloride is regenerated. On treating orthodichlorostilbene dichloride with alcoholic potash at 100°, the *trichlorostilbene*, $C_6H_4Cl\cdot CH{:}CCl\cdot C_6H_4Cl$, is formed, and crystallises from alcohol and ether in small scales melting at 66°. By the further action of potash on this compound, *orthodichlorotolane* $C_6H_4Cl\cdot C{:}C\cdot C_6H_4Cl$, is obtained, crystallising from alcohol in colourless, rhombic plates melting at 88—89°.

J. B. T.

Condensation of Orthochlorobenzotrichloride by means of Metals. By F. Fox (*Ber.*, **26**, 653—656).—Orthochlorotrichlorotoluene, $C_6H_4Cl\cdot CCl_3$, is prepared by the prolonged action of chlorine on orthochlorotoluene at 130°; the yield is 83 per cent. of the theoretical. On heating the compound in a reflux apparatus with benzene and finely divided copper for 25 hours, *orthodichlorotolane dichloride*, $C_6H_4Cl\cdot CCl{:}CCl\cdot C_6H_4Cl$ is obtained in two modifications, which may be separated by crystallisation from light petroleum. The more sparingly soluble isomeride is deposited in needles which melt at 172°; it boils at 209° under a pressure of 18 mm., and at 354° under ordinary pressures, being converted into the second modification to the extent of 36 per cent.

The second compound crystallises in monoclinic plates melting at 125—126°, and is only obtained pure, together with the compound of

higher melting point, by the action of chlorine on orthodichlorotolane in chloroform solution (compare preceding abstract); it boils at 353—356° under the ordinary atmospheric pressure, yielding 19 per cent. of the higher-melting modification, and remains unchanged on distillation in a vacuum. Both compounds yield orthodichlorotolane by the action of zinc dust at 200°. From the general properties of these compounds, the higher-melting modification is regarded as the plane symmetrical, $\begin{matrix}C_6H_4Cl\cdot CCl\\ \|\\ C_6H_4Cl\cdot CCl\end{matrix}$, the lower melting one as the centrisymmetrical, $\begin{matrix}C_6H_4Cl\cdot CCl\\ \|\\ ClC\ C_6H_4Cl\end{matrix}$. This view is confirmed by the fact that the former is more readily acted on by silver than the latter.

J. B. T.

Diresorcinol. By E. Selch (*Monatsh.*, **14**, 1—7).—Barth and Schreder (Abstr., 1879, 633) regarded the diresorcinol which they obtained by fusing resorcinol with soda as 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl, but were not able to give any proof of the relative position of the hydroxyl groups. The author endeavoured to obtain evidence as to the correctness of their view by subjecting the phenol and its tetrethyl ether to oxidation, but could not succeed in obtaining a sufficient quantity of any product for analysis. Towards sulphuric acid, diresorcinol behaves in a manner which varies according to the temperature at which the reaction is carried out; when added to 6—7 parts of sulphuric acid at 150—160°, it yields *diresorcinolsulphone*, $C_{12}H_4SO_2(OH)_4$; this crystallises in colourless, silky needles, is almost insoluble in water, and carbonises above 300° without melting. Its *tetracetyl* derivative also forms silky needles, and melts at 256°. With cold sulphuric acid, diresorcinol is converted into a *disulphonic acid*, which has not been obtained pure; its *lead* salt,

$$C_{12}H_4(OH)_4(SO_3)_2Pb + 4H_2O,$$

crystallises in pale-brown prisms united in small druses.

H. G. C.

Stereoisomeric Benzamarones. By E. Knoevenagel and R. Weissgerber (*Ber.*, **26**, 436—441).—Benzamarone was prepared by Japp and Klingemann's method (Abstr., 1889, 275). Assigning to it the formula $COPh\cdot\overset{*}{C}HPh\cdot CHPh\cdot\overset{*}{C}HPh\cdot COPh$, it is seen to contain two asymmetric carbon atoms, namely, those marked with an asterisk, and the authors have succeeded in separating it into two isomerides. The crude substance, mixed into a thin paste with alcohol, is digested on the water-bath for half an hour. The resinous constituents and *benzylidenedeoxybenzoïn* (next abstract) are thereby dissolved. The residue is boiled for 3—4 hours with 85 per cent. acetic acid, when *isobenzamarone* separates from the filtrate on cooling. Benzamarone melts at 218—219°, and isobenzamarone resembles it in crystalline form, but is more readily soluble in alcohol, glacial acetic acid, and benzene, and melts at 179—180°. Both isomerides are structurally identical; they give the same pentaphenylpyridine (m. p. 239—240°) when heated in aqueous alcoholic solution with hydroxylamine hydrochloride at 180°.

A. R. L.

Benzylidenedeoxybenzoïn. By E. KNOEVENAGEL and R. WEISSGERBER (*Ber.*, **26**, 441—446).—Benzylidenedeoxybenzoïn,

$$CHPh:CHPh\cdot COPH,$$

is one of the products in the preparation of benzamarone (preceding abstract). The best yield is obtained when a solution of potash (2 grams) dissolved in alcohol (5 c.c.) and water (5 c.c.), is added to a cooled solution of deoxybenzoïn (5 grams) in benzaldehyde (25 grams) and an equal volume of alcohol, and the mixture allowed to remain for 2—3 days. It forms white needles, and melts at 100°. When heated with an excess of deoxybenzoïn, benzamarone is formed; whilst if it is heated at 180° with hydroxylamine hydrochloride and alcohol, it yields a *compound* which crystallises in silky needles, melts at 208—209°, and, since it is insoluble in alkalis, has, perhaps, the constitution $\begin{matrix} N{=}CPh \\ | \\ O\cdot CHPh \end{matrix}\!>\!CHPh$. The *hydrazone*, $\begin{matrix} CPh{-}CHPh \\ | \quad\quad || \\ CHPh\cdot N\cdot NHPh \end{matrix}$, is obtained by heating benzylidenedeoxybenzoïn with phenylhydrazine. Benzylidenedeoxybenzoïn and benzyl cyanide react in the presence of a small quantity of alcoholic soda, forming *benzoyltriphenylbutyronitrile*, $COPh\cdot CHPh\cdot CHPh\cdot CHPh\cdot CN$, which melts at 205—210°, and appears to be resolvable into two stereoisomerides of higher and lower melting point; the same compound is obtained from a mixture of deoxybenzoïn, α-phenylsuccinonitrile, and sodium ethoxide.

A. R. L.

Condensation of Benzaldehyde with Deoxybenzoïn. By F. KLINGEMANN (*Ber.*, **26**, 818—820).—A preliminary notice, published on account of the appearance of papers by Knoevenagel, Weissgerber, and Klages (preceding abstracts). If sodium ethoxide is used as the condensing agent, four distinct products may be obtained, according to the conditions of the experiment:—(1) benzamarone, $C_{35}H_{28}O_2$; (2) benzylidenedeoxybenzoïn, $C_{21}H_{16}O$; (3) a compound, $C_{21}H_{16}O$, of unknown constitution, melting at 88—89°; (4) amaric acid, $C_{23}H_{22}O_3$, or its anhydride, $C_{23}H_{20}O_2$.

When benzamarone is distilled, it yields deoxybenzoïn, and the two isomeric substances $C_{21}H_{16}O$. That melting at 101° is an unsaturated ketone (benzylidenedeoxybenzoïn), for when reduced it yields a dihydro-product (melting at 118°), probably benzaldeoxybenzoïn, and, with phenylhydrazine, a phenylhydrazone melting at 166—167°; with deoxybenzoïn, under the influence of sodium ethoxide, it yields benzamarone. The isomeric substance melting at 88—89° is neither a ketone nor an alcohol, for it does not react either with phenylhydrazine or with acetic anhydride; it cannot be converted into benzamarone, but it can be, indirectly, into benzylidenedeoxybenzoïn.

By the action of hydrochloric acid on a mixture of deoxybenzoïn and benzaldehyde there were obtained: (1) a compound, $C_{21}H_{17}OCl$ melting at 172°; (2) an isomeric compound melting at 135°; (3) benzylidenedeoxybenzoïn; and (4) its isomeride, $C_{21}H_{16}O$. Benzylidenedeoxybenzoïn is converted into (1) and some of (2) by the action of hydrochloric acid; its isomeride, $C_{21}H_{16}O$, yields only (1).

C. F. B.

Condensation of Chlorobenzile with Phenol and with Mono- and Di-methylaniline. By S. KEMPINSKI (*Bull. Soc. Chim.* [3], **7**, 608—610).—When Zinin's chlorobenzile (*Annalen*, **119**, 178) is heated at 60—65° with phenol (2 mols.) and some zinc chloride, hydrogen chloride is evolved, and an amorphous, red compound, soluble in alkalis, and melting at about 93°, is obtained; it is probably a *dihydroxybenzopinacolin*, $COPh{\cdot}CPh(C_6H_4{\cdot}OH)_2$.

Under the same conditions, there is obtained from methylaniline a green colouring matter, which dyes cotton directly, and from dimethylaniline a blue colouring matter, which dyes wool and mordanted cotton. A. R. L.

Reduction of Benzilehydrazone. By A. PURGOTTI (*Gazzetta*, **22**, ii, 611—613).—In this preliminary note the author states that the reduction of benzilehydrazone by zinc dust and acetic acid yields a liquid base which is most probably *amidodibenzyl*,

$$NH_2{\cdot}CHPh{\cdot}CH_2Ph.$$

The *sulphate* is obtained in large crystals, and is extremely soluble in alcohol; the *hydrochloride* forms white needles, and the platinochloride separates from its boiling aqueous solution in golden laminæ. W. J. P.

Benzileoximes. By K. AUWERS and M. SIEGFELD (*Ber.*, **26**, 788—797).—An amplification of a previous preliminary notice (Abstr., 1892, 1470), with some additions. It is not true, as Minunni and Ortoleva state (this vol., i, 97), that α-benzileoxime only reacts with phenylhydrazine at 150—160°, and then yields benzilediphydrazone. As before said, they react when heated at 30—40° in alcoholic solution acidified with acetic acid, and benzileoximehydrazone is formed. The other monoxime does not give this reaction; in general, it reacts much less readily than the α-oxime. It should be noted that the authors once more apply to this second oxime, which has been known for some time now as the γ-oxime, the original name of β-monoxime. The *acetyl derivative of benzileoximehydrazone*, the melting point of which was given as 109°, melts at 113° when precipitated from chloroform solution by the addition of light petroleum; after crystallisation from hot alcohol or ether, it melts at 121—122°. Perhaps these are physically isomeric modifications.

Some salts of the benzilemonoximes with bibasic acids have been prepared. These exist in two forms, represented by the formulæ

α, $\begin{matrix} CPhO.C{\cdot}Ph \\ \| \\ N{\cdot}O{-}(R){-}O{\cdot}N \end{matrix}$ $\begin{matrix} Ph{\cdot}C{\cdot}CPhO \\ \| \\ N{\cdot}O{-}(R){-}O{\cdot}N \end{matrix}$, and β, $\begin{matrix} Ph{\cdot}C{\cdot}CPhO \\ \| \\ N{\cdot}O{-}(R){-}O{\cdot}N \end{matrix}$ $\begin{matrix} CPhO{\cdot}C.Ph \\ \| \\ N{\cdot}O{-}(R){-}O{\cdot}N \end{matrix}$.

They are prepared by treating the dry sodium salts of the corresponding oximes (suspended in benzene) with the acid chloride. They are decomposed by alkalis into the acids and the original oximes, the α-salts much more readily than the β- ones. The *carbonates* [(R) = CO in the above formulæ] from carbonyl chloride and the sodium salts of the α- and β-oximes respectively form lustrous, white needles; the α-salt melts at 122°, the β- at 163°. The *succinates*

[(R) = $CO\cdot CH_2\cdot CH_2\cdot CO$], from succinic chloride, and the sodium salts of the respective monoximes, form small, prismatic, colourless crystals; the α-salt melts at 164°, the β- at 195°. C. F. B.

Oximes. By A. Claus (*J. pr. Chem.* [2], **47**, 139—151).—A criticism on the most recent papers of Minunni (this vol., i, 86, 89, 92, 97; compare Abstr., 1892, 1080). A. G. B.

Compounds containing the Group $C_2N_2O_2$. By A. Angeli (*Ber.*, **26**, 527—530).—*Dibenzoylglyoxime*, $NOH{:}CBz\cdot CBz{:}NOH$, is obtained by reducing the corresponding peroxide, $\begin{matrix}CBz-CBz\\ \|\quad\ |\\ NO\cdot NO\end{matrix}$ (obtained by the action of nitric acid on acetophenone) with zinc dust and acetic acid. It crystallises in lustrous needles, and melts at 168° with decomposition. When treated with cold concentrated nitric acid, it is reconverted into the peroxide, which melts at 87° and has all the properties assigned to it by Hollemann (*Ber.*, **21**, 2835).

Dibenzoylazoxazole, $\begin{matrix}CBz\cdot CBz\\ \|\quad\ \|\\ N\cdot O\cdot N\end{matrix}$, obtained by treating dibenzoylglyoxime with acetic anhydride, crystallises in large, colourless prisms, and melts at 118°. The *dioxime*, $C_{16}H_{12}N_4O_3$, crystallises in white needles, melts at at 179°, dissolves easily in potash, and when treated in alkaline solution with potassium ferricyanide is converted into a compound of the composition $C_{16}H_{11}N_3O_2$, which melts at 221°. The *dihydrazone* crystallises in small, yellow needles, and melts at 172°.

Diphenyltetraketoxime, $C_6H_5\cdot[C{:}NOH]_4\cdot C_6H_5$, is obtained by the prolonged action of an excess of hydroxylamine hydrochloride on a cold alkaline solution of dibenzoylglyoxime. It is a white powder and melts at 225°. E. C. R.

β-Hydroxynaphthoic acid (m. p. 216°). By H. Hosaeus (*Ber.*, **26**, 665—673).—*Naphthophosphonic chloride*, $POCl_2\cdot O\cdot C_{10}H_6\cdot COCl$, is formed by the action of phosphoric chloride on hydroxynaphthoic acid; it crystallises from light petroleum in colourless needles, melts at 63°, and is extremely unstable. *β-Naphthophosphonic acid*, $PO(OH)_2\cdot O\cdot C_{10}H_6\cdot COOH$, is obtained by treating the preceding compound with water; it is insoluble in light petroleum, melts at 174°, and is decomposed by prolonged heating at 110°. The aqueous solution, on boiling, is resolved into β-hydroxynaphthoic acid and phosphoric acid.

β-Chloronaphthoic acid is prepared by heating the naphthoic acid (1 mol.) with phosphoric chloride (3·5 mols.) for eight hours at 180°, or by distillation of the naphthoic acid with 8 parts of phosphoric chloride; it crystallises in yellow needles, and melts at 216°. The *calcium salt* crystallises with 2 mols. H_2O.

β-Chloronaphthoic acid, on reduction with sodium amalgam, yields α-naphthoic acid (m. p. 160°).

Hemimellitic acid is formed by the oxidation of β-hydroxynaphthoic acid with potassium permanganate in alkaline solution.

β-Hydroxysulphonaphthoic acid, $COOH{\cdot}C_{10}H_5(OH){\cdot}SO_3H + 4H_2O$, crystallises from dilute hydrochloric acid in pale yellow needles. The *barium salt* crystallises in colourless needles with 5 mols. H_2O.

Dihydroxynaphthoic acid, $C_{10}H_5(OH)_2{\cdot}COOH + H_2O$, is prepared by fusing the above sulphonic acid with potash at 260°, and crystallises from water in yellow, lustrous needles melting at 265°; it is completely removed from solution by treatment with large quantities of animal charcoal, reduces silver solution at ordinary temperatures and alkaline copper solution on gently warming. The *diacetate* is crystalline, and melts at 188°. The *ethylic* salt is deposited in needles which melt at 148—150°. All attempts to eliminate the carboxyl group from hydroxysulphonaphthoic acid were unsuccessful.

The above results show that hydroxynaphthoic acid (m. p. 216°) is a heteronucleal compound, but it remains uncertain whether its constitution is COOH : OH = 1′ : 2 or 4′ : 2. J. B. T.

The Azines and Eurhodoles obtained from Dihydroxydiketotetrahydronaphthalene. By T. Zincke (*Ber.*, **26**, 613—623).—The following experiments show that the compounds obtained by the mutual action of dihydroxydiketotetrahydronaphthalene and orthodiamines are not ββ-naphthalene derivatives as previously supposed (Abstr., 1892, 859), but belong to the αβ-series; the two eurhodoles, melting at 169—170° and 183—184° respectively, prepared from orthotoluylenediamine and the above-mentioned diketo-compound, have, therefore, in all probability, constitutions analogous to those of the corresponding compounds prepared from phenylenediamine in the manner now to be described.

Naphthaphenazine oxide, $O<\begin{matrix}CH{\cdot}C_6H_4{\cdot}C{:}N\\ |\\ CH\text{——}C{:}N\end{matrix}>C_6H_4$, is produced when dihydroxydiketotetrahydronaphthalene is treated with orthophenylenediamine in alcoholic solution; it crystallises in small, yellowish, spherical aggregates of needles, melts at 186—187° with previous softening, and is not acted on by alkalis.

β-Hydroxynaphthaphenazine, $\begin{matrix}CH{\cdot}C_6H_4{\cdot}C{:}N\\ \|\\ C(OH)\text{—}C{:}N\end{matrix}>C_6H_4$ (*β-naphtheurhodole*), is obtained when the preceding compound is boiled with acetic acid or warmed with alcoholic hydrochloric acid, the solution diluted with water, and treated with ammonia until feebly alkaline; it crystallises in slender, intensely yellow needles, melts at 197—198°, and has both acid and basic properties. The *sodium* derivative crystallises in small, dirty-violet needles, and is only very sparingly soluble in water, but dissolves freely in alcohol, yielding a violet solution. The *hydrochloride* and the *sulphate* are brownish-red, crystalline compounds, and are only stable in presence of acids, being decomposed by water; the *platinochloride* is a reddish-brown, insoluble compound. The *acetyl* derivative, $C_{18}H_{12}N_2O_2$, crystallises in yellow needles, melts at 188—189°, and dissolves in concentrated hydrochloric acid with an orange-red coloration, yielding a salt which is decomposed by water;

in its hydrochloric acid solution, platinic chloride produces a sparingly soluble, red, crystalline precipitate. The *methyl* derivative, $C_{17}H_{12}N_2O$, is formed, together with large quantities of a yellow, insoluble modification of β-hydroxynaphthaphenazine, when the hydroxy-compound is treated with methylic iodide and methyl alcoholic soda; it crystallises in slender, yellow needles, melts at 158°, and is not acted on by alkalis; its *hydrochloride* crystallises in red needles, is immediately decomposed by water, and forms a brownish, granular *platinochloride*; its *bromo*-derivative crystallises in small, yellow needles, and melts at 204°.

α-Anilido-α-hydroxynaphthaphenazine, $C_{22}H_{17}N_3O$, is formed when naphthaphenazine oxide is boiled with excess of aniline in alcoholic solution. It crystallises in small, yellow needles, melts at 204—205°, and is readily decomposed when boiled with acids or when heated above its melting point, being converted into aniline and β-hydroxynaphthaphenazine; it is turned blue by hot alcoholic soda.

The compound of the composition $C_{22}H_{18}N_4O$, obtained by treating naphthaphenazine oxide with orthophenylenediamine under like conditions, is a yellow, granular powder, melts at 200°, and is only very sparingly soluble in the ordinary organic solvents; it readily undergoes decomposition on treatment with acids or when heated above its melting point, yielding β-hydroxynaphthaphenazine and orthophenylenediamine.

When naphthaphenazine oxide is heated with zinc dust in a stream of hydrogen, it yields a naphthaphenazine melting at 140—141°, identical with that obtained from the azo-derivative of β-phenylnaphthylamine.

The α-eurhodole obtained by the condensation of orthophenylenediamine and hydroxynaphthaquinone is readily converted into an acetyl derivative of the composition $C_{18}H_{12}N_2O_2$; this compound crystallises in yellowish needles, melts at 217°, and is insoluble in hydrochloric acid, which imparts to it a reddish-yellow colour.

F. S. K.

Paranthracene. By C. E. Linebarger (*Amer. Chem. J.*, **14**, 597—602).—When anthracene, in solution, is exposed to direct sunlight, paranthracene is formed, and separates out. If the solvent is benzene, toluene, xylene, or ethylbenzene, the solution remains colourless; if it is alcohol, acetic acid, ethylic benzoate, or benzene bromide (?), the solution becomes light yellow; whilst if it is chloroform, ethylenic bromide, or carbon bisulphide, it becomes black. In the last two cases, moreover, no paranthracene is formed, probably because the solvent itself undergoes decomposition.

For the preparation of paranthracene, xylene is the best solvent; a short exposure is then sufficient to bring about complete conversion of the anthracene. Beckmann has shown, by cryoscopic methods, that paranthracene has the formula $C_{28}H_{20}$; the author suggests that the bond between the two central carbon atoms of anthracene becomes loosed, and that two molecules then unite by the affinities thus set free, forming paranthracene.

C. F. B.

Friedel-Crafts Reaction in the Anthracene Series. By C. E. Linebarger (*Amer. Chem. J.*, **14**, 602—604).—Attempts to prepare phenylanthracenes by heating bromanthracene, dibromanthracene, $C_6H_4<\begin{matrix}CBr\\CBr\end{matrix}>C_6H_4$, and dichloranthracene, respectively, with benzene, in the presence of aluminium chloride, were unsuccessful; hydrogen bromide was indeed evolved, but no crystalline product, except anthracene itself, could be isolated. Anthracene, moreover, does not react with carbonyl chloride in carbon bisulphide solution in the presence of aluminium chloride. C. F. B.

Valency of the Dextroterpenes in Russian Turpentine. By A. Stschukareff (*J. pr. Chem.* [2], **47**, 191—196; compare Tilden, Trans., 1888, 879).—The author made several series of experiments on the absorption of bromine by pinene. Chloroform or carbon tetrachloride was used as a solvent, and the solution was either covered with a layer of water or contained in a flask provided with means for preventing the escape of hydrogen bromide. The bromination was effected either by adding a solution of bromine in the same solvent until a permanent pale yellow coloration was obtained, or by adding excess of bromine and titrating back with sodium thiosulphate. The hydrogen bromide was titrated in the aqueous solution by alkali. The results are tabulated, and the following conclusions deduced from them:—(1.) When bromine is added until coloration is produced, only 1 mol. of bromine reacts immediately with the pinene. (2.) When an excess of bromine is added, the pinene takes up 2 mols. (compare Tilden, *loc. cit.*). (3.) In both cases, hydrogen bromide is eliminated, but in smaller quantity than 1 mol., so that the action of the second molecule of bromine seems to occur according to the equation $C_{10}H_{16}Br_2 + Br_2 = C_{10}H_{15}Br_3 + HBr$. (4.) The dextroterpene in Russian turpentine may be regarded as a quadrivalent hydrocarbon, capable of combining with 2 mols. of bromine, to form a bromide which is very unstable, and rapidly loses a part of its bromine as hydrogen bromide, yielding a camphene bromide.

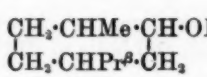
A. G. B.

Action of Acetic and Formic acids on Terebenthene. By Bouchardat and Oliviero (*Compt. rend.*, **116**, 257—259).—Mixtures of terebenthene, acetic acid, and water, in various proportions, were allowed to remain in contact in sealed tubes at the ordinary temperature for three years. In all cases there is partial conversion of the terebenthene into an isomeric, optically-active terpilene, and with the lower proportions of water, traces of terpin are formed, but the only other product is terpilenol acetate, $C_{10}H_{16}{\cdot}C_2H_4O_2$. Neither borneol nor isoborneol is formed. As the proportion of water increases, the rate and limit of the combination of the acid with the hydrocarbon diminishes, and when the mixture contains 25 molecular proportions of water to 1 molecular proportion of terebenthene and of acetic acid there is no combination.

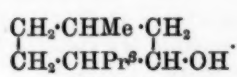
Similar experiments with formic acid show that in this case also the rate and limit of combination decrease as the proportion of water

increases, and there is no reaction when 25 molecular proportions of water are mixed with 1 molecular proportion each of terebenthene and formic acid. Formic acid is, however, more energetic in its action than acetic acid, and in this respect is comparable to the inorganic acids. When the proportion of water is low, and the acid is in excess, there is at first formation of terpilenol formate, but this is attacked by the excess of formic acid with production of inactive diterpilene, a small quantity of inactive terpilene, and traces of a formate, which, on hydrolysis, yields an active borneol. With equal molecular proportions of hydrocarbon, acid, and water, a considerable quantity of terpin is formed, together with terpilene, having a rotatory power of $\alpha_D = -23° 50'$, and terpilenol formate of feeble rotatory power. The same products are obtained in different proportions when the proportion of water is higher. C. H. B.

Orientation in the Terpene Series. By A. Baeyer (*Ber.*, **26**, 820—826).—*Dihydrocarveol*, obtained by reducing carvole with sodium in alcoholic solution, yields with acetic anhydride an *acetate* boiling at 232—234° (corr.). This takes up hydriodic acid, and the resulting hydriodide, when reduced with zinc-dust and acetic acid, yields tetrahydrocarveol acetate, which, on saponification, yields tetrahydrocarveol, and this, on oxidation with dichromate and sulphuric acid, is converted into the corresponding ketone, *tetrahydrocarvole*. This boils at 222—223° (corr.), and can be left in contact with permanganate for two minutes without being attacked; the *oxime* forms needles melting at 99—101°; *the hydrogen sulphite compound* is decomposed even by cold water. It is itself reduced by sodium to *tetrahydrocarveol*, a thick oil, which decomposes when distilled, but is very stable towards permanganate. Its formula follows from the known constitution of carvole; there is then only one possible formula left for its isomeride, menthol.

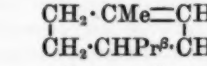


Tetrahydrocarveol.

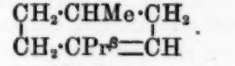


Menthol.

If tetrahydrocarveol be converted by treatment with hydrobromic acid into its bromide, and this is heated with quinoline, *carvomenthene*, boiling at 175—176° (corr.), is obtained. It yields a dibromide, and is isomeric with the menthene obtained from menthol; the formula of the two substances must be those given below, for did the bromine atom in the bromide eliminate a hydrogen atom from the neighbouring CH_2 group, both tetrahydrocarveol and menthol would yield the same unsaturated hydrocarbon.



Carvomenthene.



Menthene.

When limonene hydriodide, or, rather, the product of the action of

hydriodic acid (1 mol.) on limonene, is reduced with zinc-dust and acetic acid, limonene is regenerated as dipentene. The dihydriodide, under similar circumstances, yields an unsaturated hydrocarbon, which is, perhaps, identical with carvomenthene. Terpineol hydriodide loses hydriodic acid. *Terpineol methyl ether* was incidentally prepared, by heating terpineol and methylic iodide in toluene solution with the liquid alloy of sodium and potassium. It boils at 207—209°, and is converted into dipentene dihydrobromide by an acetic acid solution of hydrobromic acid, even in the cold. C. F. B.

Hydroxymethylene Compounds. By L. Claisen (*Ber.*, **26**, 725—729).—In preparing the benzoate of hydroxymethylenecamphor by treating hydroxymethylenecamphor with sodium ethoxide and benzoic chloride, the author finds that a good yield is obtained only when an absolute ethereal solution and sodium ethoxide free from alcohol are employed. When an alcoholic solution of sodium ethoxide is employed, heat is developed, and ethylic benzoate and the ethyl ether of hydroxymethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}OEt$, are formed. The reaction takes place as follows:—The sodium ethoxide and benzoic chloride produce ethylic benzoate and sodium chloride, and the small excess of benzoic chloride which is present forms hydrogen chloride with the alcohol; then the latter effects a simple etherification of the hydroxymethylenecamphor with the alcohol. The methyl and ethyl ethers of hydroxymethylenecamphor are easily obtained by saturating the alcoholic solution with hydrogen chloride.

The methyl ether is not an oil, as stated by v. Pechmann, but a solid, which melts at 40°.

Thus, the alkyl ethers of hydroxymethylenecamphor may be obtained in three ways: (1) by etherification with alcohol and hydrogen chloride; (2) from the sodium salt and alkylic iodide; (3) from the chloride and sodium alkyloxides.

The *phenyl ether*, $C_{10}H_{14}O{:}CH{\cdot}OPh$, obtained from the chloride and sodium phenoxide, is a viscid, colourless liquid, and boils at 214° under 13 mm. pressure.

The chloride and sodium derivative of hydroxymethylenecamphor react very easily, and yield the *anhydride* $(C_{10}H_{14}O{:}CH)_2O$, which melts at 188—189°. E. C. R.

Aldehydes from Terpenes. By A. Etard (*Compt. rend.*, **116**, 434—436).—Camphene, prepared by heating solid terebenthene hydrochloride with excess of lead monoxide at 110° for 24 hours, was dissolved in carbon bisulphide, and gradually mixed with two molecular proportions of chromyl dichloride, also dissolved in carbon bisulphide. An abundant precipitate is formed of the composition $C_{10}H_{16},2CrO_2Cl_2$, and when this is treated with water, and the solution agitated with carbon bisulphide or ether, the aldehyde is obtained. The resinous products consist chiefly of chromium camphenate.

Camphenaldehyde, $C_{10}H_{14}O$, is a solid substance, resembling camphor in appearance and consistency, and with the same property of gyratory motion on water. It is optically inactive, melts at 67°, and boils at

220°. It reduces ammoniacal silver solutions, and when exposed to air yields camphenic acid.

Camphenic acid, $C_{10}H_{14}O_2$, is volatile in water vapour, and crystallises in the condensed liquid. It melts at 65°, boils at 263—264° (uncorr.), dissolves in warm water, and forms soluble salts with magnesium, barium, calcium, and manganese, and insoluble white salts with lead, zinc, cadmium, and silver. When distilled with lime, it yields gases of the C_nH_{2n} series, hydrogen, and liquid hydrocarbons, boiling between 80° and 230°, and hence it would seem that camphenic acid is a derivative of propionic acid, and not of benzoic acid.

Terebenthene aldehyde can be obtained in the same way, and the dextro- or lævo-rotatory power of the hydrocarbon is transferred to the aldehyde. Terebenthene aldehyde boils at 205—207° under ordinary pressure; sp. gr. at 22° = 0·961. It reduces ammoniacal silver solutions, reacts with phenylhydrazine, and gives the characteristic violet coloration with a solution of magenta, decolorised by sulphurous acid (compare Abstr., 1880, 467; Trans., 1889, **45**; *Ber.*, **23**, 1070). C. H. B.

Camphorone. By W. Koenigs and A. Eppens (*Ber.*, **26**, 810—811; compare Abstr., 1892, 626).—*Camphorone oxime*, $C_8H_{14}{\cdot}C{:}NOH$, is obtained by boiling camphorone with hydroxylamine and sodium carbonate in solution in dilute alcohol; it crystallises in dazzling, white needles, melts at 121°, and is decomposed by boiling with alkalis or acids, or when quickly heated, an odour of phorone being observable. *Camphorone phenylhydrazone*, $C_8H_{14}{\cdot}C{:}N{\cdot}NHPh$, is obtained by mixing the phorone with phenylhydrazine and acetic acid in dilute alcoholic solution; it is a reddish, unstable oil, crystallising at a low temperature. C. F. B.

Function of Camphoric acid. By A. Haller (*Compt. rend.*, **116**, 121—123).—Phenylic isocyanate, at a temperature not exceeding 115°, acts on camphoric acid in the same way as on phthalic and succinic acids (Abstr., 1892, 1204), and yields camphoric anhydride melting at 216—217°, diphenylcarbamide, and carbonic anhydride. If, however, the tube containing the mixture is heated at 200°, the diphenylcarbamide and camphoric anhydride react with formation of symmetrical diphenylcamphoramide and carbonic anhydride. Diphenylcamphoramide can also be produced by heating a mixture of diphenylcarbamide and camphoric anhydride at 200°, but the reaction is not complete, and the diphenylcamphoramide is always mixed with unaltered diphenylcarbamide which can only be separated with difficulty. In order to obtain the pure amide, the crude product is dissolved in alcoholic potash, evaporated to dryness, and heated to incipient fusion, when the diphenylcarbamide is decomposed, but the greater part of the diphenylcamphoramide remains unaltered, and is crystallised from alcohol after removal of the potash by means of water.

Diphenylcamphoramide, $C_8H_{14}(CO{\cdot}NHPh)_2$, crystallises from alcohol in confused needles which melt at 221—222°, and dissolve in methyl alcohol, chloroform, and ether, but are insoluble in benzene, water,

and solutions of alkalis. It is not attacked by boiling alcoholic potash, but is partially decomposed in sealed tubes at 140—150°, with formation of phenylcamphoramic acid and aniline.

Phenylcamphoramic acid is best obtained by dissolving diphenylcamphoramide in alcoholic potash, evaporating to dryness in a silver crucible, and heating carefully to fusion as long as aniline is given off. The residue is dissolved in water, the acid liberated by the addition of an inorganic acid, and extracted with ether. It forms small, rectangular octahedra, melts at 196°, and is soluble in ether, alcohol, and potash solution, but almost insoluble in water. The isomeride obtained by Laurent by heating camphoric anhydride with aniline crystallises in needles, and melts at 209°.

The acid obtained by the author corresponds with the alkylic hydrogen salts of hydrolysis; that obtained by Laurent corresponds with the alkyl hydrogen salts obtained by direct etherification (compare Abstr., 1892, 1346).

If diphenylcarbamide and camphoric acid are heated together at 220—250°, aniline is given off, and phenylcamphoramide melting at 119° is obtained. Above 200°, therefore, diphenylcarbamide acts on camphoric anhydride in the same way as on phthalic and succinic anhydrides (*loc. cit.*).

When orthoditolylcarbamide and camphoric anhydride are heated together at 220°, in molecular proportion, *ditolylcamphoramide* is obtained; it forms small, white crystals melting at 218°.

Tetraphenylcarbamide has no action on camphoric anhydride at 220—250°.

Phenylic isocyanate, when heated at 100° with benzoic acid in molecular proportion, yields benzoic anhydride, diphenylcarbamide, and small quantities of benzanilide. If equal molecular proportions of benzoic anhydride and diphenylcarbamide are heated in sealed tubes, benzanilide is obtained in theoretical quantity. Orthotoluic acid behaves in the same way as benzoic acid.

Phenylic isocyanate is a dehydrating agent of special value in the preparation of anhydrides such as those of the acrylic series.

C. H. B.

Action of Alkali Alkyloxides on Camphoric Anhydride and other Anhydrides. By P. Cazeneuve (*Compt. rend.*, **116**, 148—151).—5 grams of sodium is dissolved in alcohol, and 20 grams of camphoric anhydride is gradually added to the solution. An energetic reaction takes place, and if the product is poured into water and subsequently acidified with hydrochloric acid, orthoethylic hydric camphorate is obtained. The alkali alkyloxide simply combines with the camphoric anhydride, with rupture of the anhydride chain. The sodium salt can be obtained as a non-crystallisable, very deliquescent syrup, very soluble in water or absolute alcohol. The methylic and amylic salts are obtained in a similar way. The latter is separated by means of light petroleum, and forms a very viscous, colourless liquid which decomposes when heated above 250°, even under reduced pressure.

Phenol under similar conditions seems to yield a camphorate.

Alkali alkyloxides react readily with phthalic and succinic anhydrides, lactide, and coumarin, but on the addition of water or alcohol of 93°, hydrolysis takes place with formation of alkali hydroxide, and disodium phthalate, succinate, or lactate is obtained. Coumarin with sodium ethoxide yields sodiocoumarin and ethyl alcohol.

It follows that the alkylic salts of camphoric acid are less easily hydrolysed than those of phthalic and succinic acids, and camphoric anhydride is neither a lactide nor a coumarin (compare Trans., 1892, 1088—1096). C. H. B.

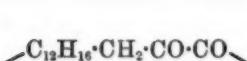
Sulphocamphylic acid. By W. Koenigs and J. Hoerlin (*Ber.*, **26**, 811—817; compare Perkin, Proc., 1893, 109).—This acid, $C_9H_{16}SO_6$, is obtained by heating camphoric acid with strong sulphuric acid on the water-bath; an improved method is given for its preparation. It crystallises with $2H_2O$; two silver salts, $C_9H_{14}SO_6Ag_2$ and $C_9H_{15}SO_6Ag + H_2O$, were prepared. When the acid is heated at 210—220°, or, better, with superheated steam at 170—190°, *isolauronolic acid*, $C_9H_{14}O_2$, is obtained in white needles melting at 135°. It is a weak acid; its *calcium* and *potassium salts*, $(C_9H_{13}O_2)_2Ca + H_2O$ and $C_9H_{13}O_2K$, were prepared. It is further stated that new crystallised compounds have been obtained by the action of bromine at 100°, of alkaline permanganate, and of nitric acid respectively; the first melts at 181—182°, and contains bromine, but no sulphur; the third melts at 198° with decomposition, and appears to have the composition $C_6H_{10}O_5$. Sulphocamphylic acid is probably a true sulphonic acid, for it is very stable when treated with nitric, hydrochloric, or hydrobromic acid, only traces of sulphuric acid being formed.

A good method is given for preparing the anhydrides of bibasic acids. It is to heat them with acetic anhydride (1 mol.) containing a little zinc chloride, and wash the product with water and cold aqueous sodium carbonate. C. F. B.

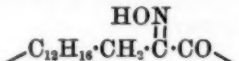
Santoninoxime and Santoninoximic acids. By J. Klein (*Ber.*, **26**, 411—414; compare this vol., i, 111—112).—A further proof is adduced of the author's view that the carbonyl group which determines the ketonic nature of santonin is situated in the side chain. The proof depends on the fact that two oximic acids, but only one oxime, are known. The oxime, prepared according to Gucci's method (Abstr., 1890, 902), contains 1 mol. H_2O, and melts at 199—201°. If prepared by hydrolysing the acetate (which melts at 165—170°), or by treating an alkaline solution of santonin with hydroxylamine hydrochloride and then acidifying, it melts at 207—209°. Both varieties have the same appearance, and are, in fact, chemically identical, for they yield identical acetyl and benzyl derivatives. The oxime is moreover a normal one, for its benzyl derivative (melting at 151—152°) yields benzyl iodide when heated with hydriodic acid. Now when santoninoxime is prepared in alkaline solution, and the solution, containing an alkaline salt of the oximic acid, is treated with ferric chloride, the violet-red colour characteristic of *syn*-oximic acids is obtained; but if the already prepared oxime is dissolved in alkali and the solution acidified and treated with ferric chloride, a

yellow colour only is produced. Hence there are two oximic acids, and that formed by direct oximation is the *syn*-oximic acid. From this it follows that the CO group of santonin is in the side chain, and further that santoninoxime, since it yields an oximic acid isomeric with the *syn*-acid, is itself an *anti*-oxime.

Santonin synoximic acid, $OH\cdot C_{12}H_{16}\cdot CH_2\cdot \overset{\overset{NOH}{\|}}{C}\cdot COOH$.

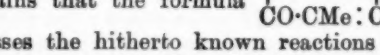


Santonin.



Santonin(anti)oxime.

It will be noted that many of the melting points quoted above differ considerably from those given by Gucci. C. F. B.

Klein's View of the Structure of Santonin. By S. Cannizzaro (*Ber.*, **26**, 786—788).—The author expresses surprise that Klein (preceding abstract) still persists in thinking that santonin contains a CO group, together with three carbon atoms in the side chain. He maintains that the formula  best expresses the hitherto known reactions of santonin, whilst many of these are not explained by Klein's formula. C. F. B.

New Series of Basic Platinum Compounds. By A. Cossa (*Gazzetta*, **22**, ii, 620—635; compare Abstr., 1890, 1218).—*Platososemiamine platosodipyridine chloride*, $2PtNH_3Cl_2,Pt(C_5H_5N)_4Cl_2$, separates on mixing solutions of platososemiamine potassium chloride and platosodipyridine chloride; it crystallises from boiling water in anorthic prisms ($a = 51° 20', \beta = 111° 18', \gamma = 88° 18'$). On treatment with a solution of potassium platinosochloride, K_2PtCl_4, a reddish precipitate of platosodipyridine platinosochloride falls, whilst platososemiamine potassium chloride remains in the mother liquor. With platosodiamine chloride, it yields the previously described salt of the composition $2PtNH_3Cl_2,Pt(NH_4)_4Cl_2$, together with platosodipyridine chloride. On adding sodium platinosochloride to its solution, platinodipyridine platinosochloride, $Pt(C_5H_5N)_4Cl_4,PtCl_2$, is precipitated.

Platososemiamine platosodiethylamine chloride,

$$2PtNH_3Cl_2,Pt(NH_2Et)_4Cl_2,$$

is deposited on mixing hot concentrated solutions of platososemiamine potassium chloride and platosodiethylamine chloride. It forms anhydrous, pleochromatic, orthorhombic prisms, and its behaviour towards reagents is quite analogous to that of the preceding salt.

Platososemipyridine platosodiamine chloride,

$$2Pt(C_5H_5N)Cl_2,Pt(NH_3)_4Cl_2,$$

is formed, together with other products, on adding pyridine to an aqueous solution of potassium platinosochloride; it is sparingly soluble in cold water, and is obtained in thin, rhombohedral laminæ. On

further treatment with potassium platinosochloride, Magnus' salt is deposited, and *platososemipyridine potassium chloride*, $Pt(C_5H_5N)Cl_2,KCl$, which crystallises in orthorhombic prisms, remains in solution. This substance is reconverted into the original double salt by the addition of platosodiamine chloride, and yields platosodipyridine chloride when treated with excess of pyridine.

Platososemipyridine platosodipyridine chloride,

$$2Pt(C_5H_5N)Cl_2,Pt(C_5H_5N)_4Cl_2,$$

is precipitated on mixing solutions of platosodipyridine chloride and platososemipyridine potassium chloride or platososemipyridine platosodiamine chloride. It is also obtained by heating platososemipyridine chloride with dilute hydrochloric acid and subsequently adding platosodipyridine chloride; the yield is, however, poor. It forms minute, doubly-refracting, acicular, yellow crystals, and, on treatment with pyridine, gives platosodipyridine chloride.

Platososemipyridine platosodiethylamine chloride,

$$2Pt(C_5H_5N)Cl_2,Pt(NH_2Et)_4Cl_2,$$

is obtained, together with platososemidipyridine chloride, on adding pyridine to hot aqueous potassium platinosochloride. It forms small, yellow prisms, and is sparingly soluble in cold water; it yields platososemipyridine platosodipyridine chloride when treated with platosodipyridine chloride, and on adding excess of potassium platinosochloride, platosodiethylamine platinosochloride separates, whilst platososemipyridine potassium chloride remains in solution.

Platososemiethylamine platosodiamine chloride,

$$2Pt(NH_2Et)Cl_2,Pt(NH_3)_4Cl_2,$$

obtained in a manner analogous to the preceding salts, forms thin, monosymmetric prisms, and is soluble in water, but insoluble in alcohol. It yields Magnus' salt and platososemiethylamine potassium chloride when treated with potassium platinosochloride; excess of ethylamine converts it into a mixture of the chlorides of platosodiamine and platosodiethylamine.

Platososemiethylamine platosodipyridine chloride,

$$2Pt(NH_2Et)Cl_2,Pt(C_5H_5N)_4Cl_2,$$

separates on mixing solutions of the preceding salt and platosodipyridine chloride. It forms yellow, fragile, opaque, orthorhombic crystals, $a : b : c = 1{\cdot}478 : 1 : 4{\cdot}542$.

The formation of the above salts confirms the view that platinum can unite with a single molecule of a base to form compounds homologous to the monammoniacal platinum derivatives previously investigated by the author. W. J. P.

So-called Quinolinium Bases. By H. Decker (*J. pr. Chem.* [2], **47**, 222—235).—The author replies to the points raised by Roser (this vol., i, 177), and criticises the analytical numbers which were published by Claus in his paper on derivatives of cinchoxinic acid (Abstr., 1892, 1488). A. G. B.

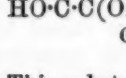
Nitro-derivatives of Isoquinoline. By A. Claus and K. Hoffmann (*J. pr. Chem.* [2], **47**, 252—266).—1- (or 4-) *Nitroisoquinoline* is the sole product of the nitration of isoquinoline with nitric acid (1 mol.) and sulphuric acid in the cold. At higher temperatures and with a larger proportion of nitric acid, the dinitro-product is obtained. 1-Nitroisoquinoline crystallises in long, slender, yellowish needles, melts at 110°, sublimes when carefully heated, and dissolves in most solvents except cold water. It is somewhat basic; the *hydrochloride*, $C_9H_6N_2O_2,HCl$, crystallises in anhydrous, prismatic, transparent, yellow tables, and melts to a black mass at 245°; the *sulphate*, $(C_9H_6N_2O_2)_2H_2SO_4$, melts with blackening at 174°; the *nitrate* becomes dark and melts at 198°; the *platinochloride* decomposes at 330°. The *methiodide*, $C_9H_6N_2O_2,MeI$, melts, with decomposition, at 205°; the *methochloride* decomposes at 225—227°. These metho-derivatives yield the same base whether decomposed by ammonia or silver oxide, and the hydrochloride of the base is identical with the methochloride (compare Abstr., 1891, 1252). Oxidation of 1-nitroisoquinoline yields nitrophthalic acid $[NO_2 : (COOH)_2 = 3 : 1 : 2]$ (m. p. 220°).

1- (or 4-) *Amidoisoquinoline*, obtained by reducing the nitro-derivative in the usual way, crystallises in colourless needles or nacreous plates, and melts at 128°. The *hydrochloride*, $C_9H_8N_2,HCl$, melts with blackening at 220°; the *platinochloride* decomposes at 200°.

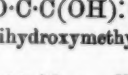
1- (or 4-) *Bromisoquinoline* is prepared from the amido-derivative by the diazo-reaction. It crystallises in colourless, vitreous needles, and melts at 80·5° (compare Abstr., 1891, 580). The *nitrate*, C_9H_6BrN,HNO_3, melts at 193°. The *nitro*-derivative crystallises in colourless needles, and melts at 140°. The *methiodide*, C_9H_6BrN,MeI, crystallises in yellow columns, and melts at 274°. When this methiodide is treated with silver oxide, it gives a strongly alkaline base which is soluble in water but insoluble in ether, and yields the original methohaloïd when treated with acids; but caustic alkalis (except ammonia) convert the methiodide into a base which is insoluble in ether and is reconvertible into a haloïd dissimilar from the original methohaloïd.

Dinitroisoquinoline forms small, yellowish, lustrous crystals, melts at 238·5°, and is sparingly soluble in alcohol; the *platinochloride* and *methiodide* have been prepared. A. G. B.

Syntheses of Isocumarin and Isoquinoline Derivatives. By P. Fritsch (*Ber.*, **26**, 419—422).—If gallacetol, obtainable from gallic acid (?) and chloracetone, is rendered anhydrous and then mixed with cooled concentrated sulphuric acid, condensation takes place, and a *trihydroxymethylisocoumarin* is formed.



Gallacetol.



Trihydroxymethylisocoumarin.

This substance crystallises in efflorescent tables. When heated in a sealed tube with alcoholic ammonia at 120—130°, NH is substituted for

the –O– atom, and a substance is formed which would be called *trihydroxymethylisocarbostyril*, according to Bamberger's nomenclature, but which the author proposes to name *trihydroxymethylisoquinolone*.

Other attempts at analogous syntheses have so far been unsuccessful. C. F. B.

Pyrazolone and some Derivatives. By R. v. ROTHENBURG (*Ber.*, **26**, 415—417; compare this vol., i, 180).—*Ethylic 4-azobenzenepyrazolone-3-carboxylate*, $NH<\begin{matrix}N=C\cdot COOEt\\ CO\cdot C:N_2HPh\end{matrix}$, was prepared by treating ethylic pyrazolone-3-carboxylate with a diazobenzene salt; it melts at 241°, forms sparingly soluble red plates, and has acid properties. By treating an alcoholic solution of the same ethylic salt with nitrous anhydride, *ethylic isonitrosopyrazolonecarboxylate*

$$[COOEt : NOH = 3 : 4]$$

was obtained; this forms yellowish, ill-defined crystals, and melts at 182°; its *silver salt* is a reddish-yellow powder. The same ethylic salt, when treated with benzaldehyde, yields *ethylic benzalpyrazolonecarboxylate* [COOEt : CHPh = 3 : 4] as a reddish-yellow, very sparingly soluble substance melting above 250°.

If pyrazolone-3-carbonylhydrazine is shaken with benzaldehyde in aqueous solution, *pyrazolonecarbonylbenzalhydrazine*

$$[CO\cdot NH\cdot N:CHPh : H_2 = 3 : 4]$$

is obtained as a white, sparingly soluble substance melting above 250°. If excess of benzaldehyde is present, *benzalpyrazolonecarbonylbenzalhydrazine* [CO·NH·N:CHPh : CHPh = 3 : 4] is formed; it is a yellowish, very sparingly soluble powder melting above 250°.

Silver pyrazolonecarboxylate [COOAg : HAg = 3 : 4] forms a white, unstable powder. The acid, when treated with a diazobenzene salt, yields *azobenzenepyrazolonecarboxylic acid* [COOH : N·NHPh = 3 : 4] as a fine powder melting above 250°. And the same acid, when suspended in alcohol and treated with gaseous nitrous acid, yields *isonitrosopyrazolonecarboxylic acid* [COOH : NOH = 3 : 4] as golden-yellow plates decomposing at 215—220°; the *silver salt* of this, containing 2 atoms of silver in the molecule, forms an orange-yellow powder which explodes when heated. Again, the same acid yields, with benzaldehyde, at 120—150°, or under the action of strong hydrochloric acid, *benzalpyrazolonecarboxylic acid* [COOH : CHPh = 3 : 4] as a yellow, amorphous powder melting at 243°. C. F. B.

Condensation Products of the Hydrazides of Ethyl Acetoacetate and Oxalacetate. By C. WALKER (*Amer. Chem. J.*, **14**, 576—586).—The hydrazide of ethylic acetoacetate,

$$COOEt\cdot CH:CMe\cdot NH\cdot NHPh,$$

can yield, under different conditions: (I) 1-phenyl-3-methyl-5-pyrazolone (Knorr, Abstr., 1887, 601; Nef, 1892, 145); (II) 1-phenyl-3-methyl-5-ethoxypyrazole, $\begin{matrix}CMe=N\\ CH:C(OEt)\end{matrix}>NPh$; and (III) ethylic

α-methylindole-β-carboxylate (Nef, Abstr., 1892, 142). The hydrazide of ethylic oxalacetate, COOEt·CH:C(COOEt)·NH·NHPh, behaves in a similar manner, except that no compound analogous to (III) has yet been obtained.

That the salt III (which is obtained by the action of strong sulphuric acid on the hydrazide and melts at 131°, and not at 134° as previously stated) has the constitution $NH<\begin{matrix}CMe\\C_6H_4\end{matrix}>C\cdot COOEt$, was proved by its having the same properties as the ethylic salt prepared, for purposes of comparison, from the α-methindole-β-carboxylic acid of Ciamician and Magnanini (Abstr., 1888, 958). It gives no coloration with ferric chloride, and is stable towards alcoholic potash, but if heated with caustic potash it loses carbonic anhydride, and forms methylketole.

The compound (II) is obtained by treating ethylic acetoacetate with phenylhydrazine hydrochloride (compare Freer, Abstr., 1892, 953, and this vol., i, 67, who describes it, probably erroneously, as a phenylmethylpyrazolone). Its properties closely resemble those of the phenylethoxypyrazole mentioned above. The *platinochloride* forms yellow, six-sided prisms melting at 191°.

When the hydrazide of ethylic oxalacetate is treated with dehydrating agents, the chief product is a compound analogous to (I), but at the same time another, analogous to (II), is formed in small quantity—in largest amount when an acetic acid solution of the hydrazide is saturated with hydrogen chloride and warmed for an hour at 60°. It crystallises in needles, melts at 83—84°, and has feebly basic properties. Its constitutional formula is $\begin{matrix}C(COOEt):N\\|\\CH=C(OEt)\end{matrix}>NPh$. The COOEt group may be hydrolysed by boiling with alcoholic potash, and *1-phenyl-5-ethoxypyrazole-3-carboxylic acid*, $C_{12}H_{12}N_2O_3$ is then obtained. This forms transparent plates or flat needles, which become opaque when dried, and melt at 152—153°; the *barium salt*, with $2H_2O$, forms colourless needles; the *calcium salt*, with $4H_2O$, rhombic plates. When the acid, or the ethylic salt, is heated with strong hydrochloric acid at 150° in a sealed tube, the OEt group is also saponified, and *1-phenyl-5-hydroxylpyrazolecarboxylic acid*, $C_{10}H_8N_2O_3$, is formed. This forms colourless needles melting at 252—253°; when heated to 230°, it loses carbonic anhydride and chars; its *silver salt*, $C_{10}H_6N_2O_3Ag_2$, forms a colourless, gelatinous precipitate. The ethylic salt, when heated at 205—230°, loses carbonic anhydride and yields *1-phenyl-5-ethoxypyrazole* as a dark red oil of feebly basic properties, which forms a *platinochloride*, $(C_{11}H_{12}N_2O)_2,H_2PtCl_6$, as pale yellow needles melting at 142—143°. C. F. B.

Benzo-3-phenylpyridazolone By R. v. Rothenburg (*Ber.*, **26** 417—419).—This substance, $\begin{matrix}CH\cdot CH:C\cdot CPh:N\\||\quad\quad|\quad\quad||\\CH\cdot CH:C\cdot CO-NH\end{matrix}$, is formed when orthobenzoylbenzoic acid, or, better, its ethylic salt, is heated with hydrazine hydrate in alcoholic solution. It forms flat needles, melts at 232°, and distils unchanged, but is decomposed by acids and alkalis into the above components. The imido-group does not react

with nitrous acid, but its hydrogen atom can be replaced by methyl if the substance is heated with methylic iodide and methyl alcohol in a sealed tube at 100°; the product forms plates which melt at 153°, and are more soluble than the mother substance. C. F. B.

Phenyluracil and its Analogues. By E. WARMINGTON (*J. pr. Chem.* [2], **47**, 201—221).—*Phenyluracil*, $OH\cdot C\begin{matrix}N=CPh\\ N\cdot C(OH)\end{matrix}>CH$, is made by heating ethylic benzoylacetate with carbamide at 170°. It crystallises in small rhombohedra, melts at 262·5°, and dissolves easily in warm alcohol, glacial acetic acid, and boiling water; it has feebly acid properties, dissolving in alkalis with formation of salts. The *silver* salt, $C_{10}H_6Ag_2N_2O_2$, was analysed, and the *calcium* salt crystallised. Strong hydrochloric acid, methylic iodide, and hydroxylamine are without action on it. When heated with phosphoric chloride, it yields *phenyldichlorometadiazine*, $CCl\begin{matrix}N:CPh\\ N\cdot CCl\end{matrix}>CH$, which crystallises in laminæ, melts at 86·5°; and is reconverted into phenyluracil when heated with strong hydrochloric acid at 160°. The latter fact confirms the constitution here ascribed to phenyluracil (which also finds support in the indifference of methylic iodide) and confutes Behrend's view (*Annalen*, **229**, 25) that these compounds are dicarbonyl derivatives. By heating phenyldichlorometadiazine with alcoholic ammonia, *phenyldiamidometadiazine hydrochloride*, $C_{10}H_{10}N_4,2HCl$, was prepared; it crystallises in lustrous needles, and decomposes at 290°.

Phenylthiouracil, $SH\cdot C\begin{matrix}N=CPh\\ N\cdot C(OH)\end{matrix}>CH$, is similarly prepared from ethylic benzoylacetate and thiocarbamide; it crystallises in bright yellow needles, melts at 253—254° (uncorr.), and dissolves in warm dilute alkalis, alcohol, and glacial acetic acid. A *silver* salt, containing 2 atoms of silver, was prepared. Strong hydrochloric acid at 180°, and fuming nitric acid at the ordinary temperature, convert it into phenyluracil.

The reaction between diphenylthiocarbamide and ethylic benzoylacetate at 180° yields benzoylacetic anilide (m. p. 107—109°; Knorr, Abstr., 1888, 1113); distillation with potash converts this substance into acetophenone, aniline, potassium carbonate, and diphenylcarbamide.

Ethylic benzoylacetate had no action on diphenylthiocarbamide in ether at 160°, or on monophenylcarbamide at 150—160°.

"Phenylimidouracil" was obtained by Jaeger (Abstr., 1891, 1007) by the mutual action of guanidine carbonate and ethylic benzoylacetate, and was found to melt at 294°. The same compound is obtained by the action of alcoholic ammonia on phenylthiouracil. When the mother liquor from the guanidine reaction was heated in a tube at 160°, and then evaporated to dryness and extracted with dilute hydrochloric acid, the hydrochloride of an isomeride of Jaeger's base was obtained. The new *base* melts at 272—274°, and crystallises in long, rhombohedral plates; it is almost twice as soluble in absolute alcohol at 26·5° as is Jaeger's base, and its hydrochloride melts at

276—277°, whereas that of "phenylimidouracil" melts at 269°. The *picrate* of the base of m. p. 294° melts at 240—241° (uncorr.); that of the other base melts at 241—242°, but each picrate yields its own base when treated with ammonia. The *nitrates* were also prepared, and found to be very similar. Both bases yield an *acetyl* derivative, which melts at 248° (uncorr.), but this derivative, when decomposed with potash, always yields the base which melts at 294°, from whichever base it may have been originally made. Strong hydrochloric acid at 190—200° converts both bases into phenyluracil and ammonium chloride. Nitrous acid also converts them into phenyluracil. The bases readily pass into each other; thus that of higher melting point is largely converted into that of lower melting point when heated with alcohol at 180°. The author is of the opinion that the two bases are to to be represented by the formulæ

$$NH_2\cdot C\begin{matrix}N:CPh\\ N\cdot COH\end{matrix}CH \text{ and } NH:C\begin{matrix}N=CPh\\ NH\cdot COH\end{matrix}CH$$

respectively, but he is at present unable to identify either of them.

A. G. B.

β-Succinylphenylhydrazide or 1-Phenyl-3:6-orthopiperazone. By A. Michaelis and R. Hermens (*Ber.*, **26**, 674—680).—The production of phenylorthopiperazone from succinic chloride and sodium phenylhydrazine (Abstr., 1892, 1494) takes place in two stages; in the cold, sodium chloride, phenylorthopiperazone, and phenylhydrazine hydrochloride are formed, and then, on heating, the phenylhydrazine hydrochloride and excess of succinic chloride react to yield a further quantity of phenylorthopiperazone and hydrogen chloride. The phenylorthopiperazone is therefore obtained by boiling a mixture of phenylhydrazine hydrochloride, succinic chloride, and benzene in a reflux apparatus as long as hydrogen chloride is evolved.

1-Phenyl-3:6-orthopiperazone, $C_2H_4\begin{matrix}CO\cdot NPh\\ CO\cdot NH\end{matrix}$, when heated with hydrochloric acid or alkalis, is converted into phenhylhydrazine and succinic acid. It distils without decomposition at 240° under 10 mm. pressure, but is converted into α-succinylphenylhydrazide when distilled under the ordinary pressure. When distilled with zinc dust, it yields aniline, α-succinylphenylhydrazide, and a viscid oil, which the authors believe to be phenylorthopiperazine. The salts of phenylorthopiperazone are soluble in water; the silver and copper salts are crystalline, the lead and barium salts gummy. The *benzoyl* compound crystallises in white leaflets, and melts at 185°. Alkyl derivatives are easily obtained by the action of alkylic iodides on the silver or sodium salts. *Phenylmethylpiperazone*, $C_2H_4\begin{matrix}CO\cdot NPh\\ CO\cdot NMe\end{matrix}$, melts at 180°. The *ethyl* compound forms colourless crystals, melts at 60·5°, is decomposed when heated with alkalis, and reduces Fehling's solution on boiling. The *benzyl* compound crystallises in colourless needles, and melts at 159°.

Ethylic phenylbenzylhydrazinesuccinate,

$$NHPh{\cdot}N(CH_2Ph){\cdot}CO{\cdot}C_2H_4{\cdot}COOEt,$$

crystallises from the mother liquor obtained in the preparation of the preceding phenylbenzylpiperazone, and melts at 79°. It is easily hydrolysed by heating with alcoholic potash, and yields *phenylbenzylhydrazinesuccinic acid*. This crystallises in long, colourless needles, melts at 142°, and energetically reduces Fehling's solution when warmed.

The authors believe that they have obtained symmetrical *benzylphenylhydrazine*, $NHPh{\cdot}NH{\cdot}CH_2Ph$, by heating the preceding compound with concentrated hydrochloric acid in a reflux apparatus. It crystallises in colourless leaflets, melts at 167—170°, and on oxidation with yellow mercuric oxide, yields an oil which is probably phenylazobenzyl, $PhN{:}N{\cdot}CH_2Ph$, together with a sparingly soluble compound melting at 200—201°. Unsymmetrical benzylphenylhydrazine also melts at 167°, but it crystallises in needles, and yields a tetrazone when treated with mercuric oxide. E. C. R.

Action of Ammonia and Hydrazine on Opianic and Phthalaldehydic acids. By C. Liebermann and A. Bistrzycki (*Ber.*, **26**, 531—540).—*Dimethoxyphthalazone* (*opiazone*), $C_6H_2(OMe)_2{<}\begin{matrix}CO{\cdot}NH\\|\\CH{:}N\end{matrix}$, is obtained by warming an aqueous solution of opianic acid, hydrazine sulphate, and sodium acetate on the water bath. It crystallises from water in beautiful, long needles, containing 1 mol. H_2O, melts at 162°, loses its water at 100°, and then melts at 166°. It dissolves both in strong hydrochloric acid and potassium hydroxide, and is precipitated on the addition of water. It is not acted on by Fehling's solution. When dissolved in concentrated sulphuric acid, and treated with nitric acid, it yields a compound crystallising in yellow needles. The *methyl* compound, obtained by the action of methylic iodide on the potassium salt, crystallises in needles, and melts at 138°. The *acetyl* derivative crystallises in needles, and melts at 158—159°.

Dichlorodihydro-opiazine, $C_6H_2(OMe)_2{<}\begin{matrix}CCl_2{\cdot}NH\\|\\CH:N\end{matrix}$, is obtained by the action of phosphorus pentachloride on the preceding compound. It crystallises in yellow aggregates, melts at 260° with decomposition, and when treated with water, or better with dilute soda, is converted into *monochloro-opiazine*, $C_6H_2(OMe)_2{<}\begin{matrix}CCl{:}N\\|\\CH{:}N\end{matrix}$. This melts at 152°, is very easily decomposed, and on reduction yields an oily base free from chlorine, which quickly turns brown.

Diopianhydrazonic anhydride, $\begin{matrix}N{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CO\\|\\N{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CO\end{matrix}{>}O$, is obtained, together with opiazone, when a solution of opianic acid, hydrazine sulphate, and sodium acetate is heated to boiling for a few minutes. It is a heavy, white, crystalline powder, melts at 225°, is insoluble in alkali, and has no action on Fehling's solution.

Phthalazone, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CH{:}N\end{matrix}$, is obtained from phthalaldehydic acid, in the same way as opiazone from opianic acid. It crystallises in long, lustrous needles, melts at 183—184°, sublimes at 100° in small prisms, and closely resembles opiazone. The *silver salt*, $C_6H_4<\begin{matrix}CO\cdot NAg\\ |\\ CH{:}N\end{matrix}$, crystallises in aggregates of microscopic needles. The *acetyl* compound crystallises in small prisms, and melts at 132—133°.

Diphthalaldehydehydrazonic acid, $N_2(CH\cdot C_6H_4\cdot COOH)_2$, is obtained by mixing cold, saturated solutions of phthalaldehydic acid and hydrazine acetate. It crystallises in pale yellow, microscopic needles, melts at 211°, is without action on Fehling's solution, and when boiled with water is converted into phthalaldehydic acid and phthalazone. The *silver* salt is obtained as a white, flocculent precipitate.

When opianic acid is heated with alcoholic ammonia for 6—8 hours at 160°, or with aqueous ammonia for 2—3 days at the temperature of boiling water, *bisdimethoxymetindolone* and *tetramethoxydihydrodiphthalyldiimide* are formed. The two compounds are separated by means of acetic acid, in which the former is insoluble.

Bisdimethoxymetaindolone, $\begin{matrix}(OMe)_2C_6H_2\cdot C & = & C-C_6H_2(OMe)_2\\ | & & | \quad | \\ OH\cdot C & = & N \quad N=C\cdot OH\end{matrix}$, is nearly insoluble in all solvents, does not melt at 340°, is a very indifferent compound, and exhibits in concentrated sulphuric acid a deep rose-red coloration and fluorescence, which changes to a beautiful blue on the addition of nitric or chromic acid.

Tetramethoxydihydrodiphthalyldiimide, $C_2H_2[<\begin{matrix}C_6H_2(OMe)_2\\ NH\text{——}CO\end{matrix}>]_2$ crystallises in small, bright yellow needles, melts at 249° with decomposition, and has feeble basic properties. With concentrated sulphuric acid, it gives a yellow solution, which does not turn blue on the addition of nitric acid.

The action of ammonia on phthalaldehydic acid is very similar to its action on opianic acid, and the two following compounds were obtained.

Bismetaindolone, $OH\cdot C<\begin{matrix}C_6H_4\\ N\text{—}\end{matrix}>C{:}C<\begin{matrix}C_6H_4\\ \text{—}N\end{matrix}>C\cdot OH$, is very sparingly soluble, crystallises in microscopic prisms, does not melt at 330°, and exhibits in concentrated sulphuric acid a yellow coloration, which changes to dirty brown on the addition of nitric acid.

Dihydrodiphthalyldiimide, $CO<\begin{matrix}C_6H_4\\ \text{—}NH\end{matrix}>CH\cdot CH<\begin{matrix}C_6H_4\\ \text{—}NH\end{matrix}>CO$, is easily soluble in acetic acid, crystallises in colourless needles, and melts at 284° with decomposition.

The authors attempted to prepare the last two compounds by heating diphthalyl with methyl alcoholic ammonia at 160°; the compound obtained, however, was diphthalylmonoimide. E. C. R.

Derivatives of Dichloroquinazoline. By A. Kötz (*J. pr. Chem.* [2], **47**, 303).—When $\beta\delta$-dichloroquinazoline (Abstr., 1889,

610) is heated with alcoholic ammonia at 150°, the *compound* $C_6H_4<\begin{matrix}C(NH_2):N\\N:C(NH_2)\end{matrix}>$ is formed; it crystallises in long, yellowish needles, and melts at 248—250°; a *platinochloride* was obtained. The corresponding *methylamine derivative* melts at 282—284°, and yields a *platinochloride*. By heating the dichloroquinazoline with an alcoholic solution of potassium hydrogen sulphide, a *dithio-derivative*, $C_8H_6N_2S_2$, is obtained; it melts above 250°, is decomposed at 260°, and gives a white precipitate with mercuric chloride. A. G. B.

Pyrazine. By L. Wolff (*Ber.*, **26**, 721—725).—Pyrazinetetracarboxylic acid, $C_4N_2(COOH)_4 + 2H_2O$, is obtained by oxidising tetramethylaldine with potassium permanganate (*Ber.*, **20**, 427). It crystallises in white leaflets, melts at 204—205° with decomposition, and gives a violet to cherry-red coloration with ferrous sulphate, which disappears on the addition of a mineral acid. The normal potassium and sodium salts are easily soluble in water; the *barium* $C_8N_2O_8Ba_2, 1\frac{1}{2}H_2O$, the *calcium*, with $2\frac{1}{2}H_2O$, and *silver salts*, with $\frac{1}{2}H_2O$, are almost insoluble. The *dipotassium* and *disodium salts*, $C_4N_2(COONa)_2(COOH)_2 + 2H_2O$, are very characteristic, and sparingly soluble in cold water. The dipotassium salt, when heated with water at 200°, yields carbonic anhydride, pyrazine, and pyrazinedicarboxylic acid.

Pyrazinedicarboxylic acid, $C_4N_2H_2(COOH)_2 + 2H_2O$, crystallises in prisms, and volatilises without melting when heated at 282°, yielding pyrazinecarboxylic acid, pyrazine, and carbonic anhydride. The *silver*, *calcium*, with $4H_2O$, and *barium* salts are sparingly soluble.

Pyrazinecarboxylic acid, $C_4N_2H_3{\cdot}COOH$, is obtained by distilling the dicarboxylic acid; it crystallises in white prisms, sublimes when cautiously heated, and at 225° is converted into pyrazine and carbonic anhydride. The *calcium*, with $4H_2O$, and *silver* salts are well-crystallised compounds.

Pyrazine, $C_4N_2H_4$, is best obtained by slowly distilling the dicarboxylic acid. It distils at 115° under 730 mm. pressure, and solidifies in the receiver to a white, crystalline mass which melts at 55°. It crystallises in large prisms, has an odour resembling that of heliotrope or fennel, and is very like tetramethylpyrazine. It is very volatile, and sublimes at the ordinary temperature when placed in a closed vessel. The *hydrochloride*, $C_4N_2H_4,HCl$, crystallises in large needles, sublimes above 135° without melting, and is very hygroscopic. The *picrate* crystallises in yellow needles, and melts at 157°. The *gold salt*, $C_4N_2H_4,AuCl_3$, crystallises in lustrous, yellow plates, and melts at 200°. The *silver salt*, $C_4N_2H_4,AgNO_3$, crystallises in small prisms, and melts at 257°. With potassium bismuthoiodide, the solution of the base in nitric acid gives a characteristic, cinnabar-red precipitate.

Pyrazine and trimethylpyrazine, when treated with sodium and alcohol, combine with 6 hydrogen atoms, and yield respectively diethylenediamine (piperazine) and tetramethylpiperazine; the latter exists in stereometric forms, of which two have been isolated in a pure state,

and a third modification obtained in small quantities, yielding a dinitroso-derivative melting at 82—86°.

α-Tetramethylpiperazine, $C_4N_2H_6Me_4 + 2H_2O$, crystallises in white needles, melts at 84° or, when anhydrous, at 46°, and boils at 171° without decomposition. The aqueous solution has a strongly alkaline reaction. The *dinitroso*-compound melts at 154°, the *dibenzoyl* compound at 245°.

β-Tetramethylpiperazine, $C_4N_2H_6Me_4$, is an oil which boils at 176°, and is easily soluble in water. The *dinitroso*-compound melts at 99°, the *dibenzoyl* compound at 173°.

Piperazine, obtained from pyrazine, is identical with diethylenediamine. The *dinitroso*-compound crystallises in indented leaflets, and melts at 156—158°. The *dibenzoyl* compound melts at 191°.

E. C. R.

Paradiazine Derivatives. By P. W. Abenius (*J. pr. Chem.* [2], **47**, 183—190; compare Abstr., 1889, 134; 1890, 268, 525).—The orientation which the author adopts for the paradiazines is expressed by the formula $R{\cdot}N<\overset{\alpha\ \beta}{C{\cdot}C}\atop{\beta\ \gamma}{C{\cdot}C}>N{\cdot}R$. Bischoff (this vol., i, 54) has obtained a compound of melting point 234°, to which he ascribes the same formula as that allotted by the author to diphenyldiketoparadiazine, obtained by the action of phosphorus and hydriodic acid on diphenyl-αγ-diketodichloroparadiazine (Abstr., 1890, 525); the latter compound, however, melts above 300°.

Diorthotolyl-αγ-tetraketoparadiazine, $\begin{matrix}CO{\cdot}CH{\cdot}N{\cdot}C_6H_4Me\\ C_6H_4Me{\cdot}N{-}CH{\cdot}CO\end{matrix}$ [N : Me = 2 : 1], is prepared by reducing diorthotolyl-αγ-diketodichloroparadiazine with phosphorus and hydriodic acid. It crystallises in aggregates of small needles or laminæ, melts at 231—232°, and dissolves in hot alcohol, benzene, acetone, and glacial acetic acid, but not in ether or water. It dissolves in fuming hydrochloric acid, and is precipitated again, undecomposed, by water. Hot concentrated alkalis decompose it with elimination of orthotoluidine and oxalic acid. It reduces ammoniacal silver oxide very easily; a reaction which it shares with all the αγ-diketoparadiazines. Attempts to displace the chlorine by hydrogen by means of nascent hydrogen proved unsuccessful.

Diorthotolyltetraketoparadiazine, $C_6H_4Me{\cdot}N{:}(CO{\cdot}CO)_2{:}N{\cdot}C_6H_4Me$ [N : Me = 2 : 1], is obtained by oxidising the diketoparadiazine with as little chromic acid as possible in cold glacial acetic acid (compare the behaviour of the diketodihydroparadiazine, Abstr., 1890, 525); it crystallises in lustrous needles or prisms, melts at 274°, and dissolves best in hot acetone. When heated with toluidine, it is converted into diorthotolyloxamide (m. p. 210°), which, together with oxalic acid and oxalorthotoluidic acid (m. p. of crystals, with 1 mol. H_2O, 83—84°; Abstr., 1886, 886), is also obtained when it is heated with dilute potash or soda. Oxidation by hot chromic acid converts it into diorthotolylparabanic acid.

A. G. B.

Oxidation of Azimidotoluene. By J. A. Bladin (*Ber.*, **26**, 545—546).—When azimidotoluene, $C_6H_3Me<\begin{matrix}NH\\N\end{matrix}>N$, is carefully oxidised with alkaline potassium permanganate, the benzene nucleus is destroyed, and the substance converted into 1 : 2 : 3-*triazoledicarboxylic acid*, $N<\begin{matrix}N{-}C\cdot COOH\\ \|\\ NH\cdot C\cdot COOH\end{matrix}$, this being the first known derivative of a triazole in which the three nitrogen atoms occupy the adjacent position. It crystallises from fuming hydrochloric acid in colourless plates or large prismatic crystals, and melts at 200° with violent evolution of gas and formation of a brown oil. It liberates carbonic anhydride from carbonates, but does not yield a nitroso-derivative. The normal salts are very soluble in water, but the acid salts crystallise well; the *acid potassium* salt, $C_4H_2N_3O_4K + H_2O$, forms colourless needles, and the *acid sodium* salt, $C_4H_2N_3O_4Na + 2H_2O$, slender needles which rapidly change into small prisms.

H. G. C.

Constitution of Nicotine. By F. Blau (*Ber.*, **26**, 628—633; compare Abstr., 1892, 1365, and Pinner, Abstr., 1892, 1497, and this vol., i, 286).—When nicotine is reduced with sodium and alcohol, it yields a very small quantity of ammonia, a rather small quantity of a substance which is non-volatile with steam, and an oil which is volatile with steam, and contains octohydronicotine and other bases.

Octohydronicotine hydrochloride, $C_{10}H_{22}N_2,2HCl$, can be isolated by fractionally distilling the oil with steam and treating the several fractions with hydrochloric acid; it is a crystalline substance, melts at 201—202°, and is extremely soluble in water. The *platinochloride* melts at 202° with decomposition; the *aurochloride* forms sparingly soluble, yellow plates, and melts at 142°; the *picrate* melts at about 285°. The *base*, $C_{10}H_{22}N_2$, is a colourless oil boiling at 259—260° (corr.). When the hydrochloride is strongly heated in a stream of hydrogen chloride, it yields a considerable quantity of a gas which has the properties of methylic chloride; nicotine hydrochloride behaves in a similar manner, a fact which shows that the base contains a methyl group in combination with nitrogen.

The constitution of octohydronicotine may be represented by the formula $C_5NH_{10}\cdot C_4H_8\cdot NHMe$, and that of nicotine by the formula $C_5NH_4\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ |\\ NMe\end{matrix}$ or $C_5NH_4\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ |\\ NMe\end{matrix}>CH_2$; such a constitution of nicotine would account most satisfactorily for its behaviour and also for that of the dibromocotinine and dibromoticonine described by Pinner, assuming that the two last-named compounds have a constitution analogous to that of nicotine.

F. S. K.

Trimethylxanthine Derivatives. By M. Gomberg (*Amer. Chem. J.*, **14**, 611—619).—When caffeïne is boiled with iodine in chloroform solution, and the product successively heated at 140—150° to remove iodine, and extracted with chloroform and carbon bisulphide, a dark,

granular powder is obtained of the composition $C_8H_{10}N_4O_2,I_8$, possibly a tetriodide of iodocaffeïne.

The action of sodium on a mixture of an alkylic haloïd and a halogen caffeïne gave no satisfactory results. Zinc ethide did not react with either chlorocaffeïne or bromocaffeïne in ethereal solution, but when it is heated at 160° with bromocaffeïne in the absence of a third substance, a compound containing bromine is formed, but was not obtained pure enough for analysis.

When chlorocaffeïne is boiled with potassium cyanide in alcoholic solution, a substance is obtained which is perhaps an amido-derivative, $C_8H_9N_4O_2{\cdot}CO{\cdot}NH_2$, resulting from the partial hydrolysis of cyanocaffeïne, $C_8H_9N_4O_2{\cdot}CN$, formed in the first instance.

C. F. B.

Mercuriodides of Organic Bases. By A. B. Prescott (*Amer. Chem. J.*, **14**, 606—611).—The mercuriodides of quinine, pyridine (boiling at 114·5°), and quinoline were prepared by precipitating solutions of the alkaloïds at 25° with a decinormal solution of potassium mercuriodide, excess of the latter being avoided. In the case of quinine, the concentration of the solution was varied, but this had no effect on the composition of the precipitate, analyses of which agree best with the formula $2C_{20}H_{24}N_2O_2,3HI,3HgI_2 + H_2O$. The pyridine precipitate had the composition $C_5H_5N,2HgI_2$; the quinoline one, C_9H_7N,HgI_2.

C. F. B.

Oxidation Products of Apocinchene. By W. Koenigs (*Ber.*, **26**, 713—721).—Cinchonine and cinchonidine, when successively treated with phosphorus pentachloride and alcoholic potash, are converted into cinchene, $C_{19}H_{20}N_2$, and this base, when boiled with concentrated hydrobromic acid, yields apocinchene, $C_{19}H_{19}NO$. The author and others (*Ber.*, **14**, 1855; Abstr., 1885, 1248, and 1888, 71) have already shown that, from apocinchene, an ethyl ether is obtained, which, when oxidised, yields a monocarboxylic acid, and that this, when boiled with concentrated hydrobromic acid, yields ethylic bromide, carbonic acid, and homapocinchene, $C_9NH_6{\cdot}C_6H_8{\cdot}OH$. Hence, the formula for apocinchene may be written $C_9NH_6{\cdot}C_6H_7Et{\cdot}OH$.

By oxidising ethylapocinchene with lead peroxide or manganese dioxide and dilute sulphuric acid, ethylapocinchenic acid, together with the two new compounds, ketoethylapocinchene and the lactone of hydroxyethylapocinchenic acid, are produced.

Ketoethylapocinchene, $C_9NH_6{\cdot}C_6H_2Et(OEt){\cdot}COMe$, melts at 104—106°, and, when boiled with concentrated hydrobromic acid, is converted into homapocinchene. The *oxime* melts at 181—184°.

The lactone of hydroxyethlapocinchenic acid,

$$C_9NH_6{\cdot}C_6H_2(OEt)\begin{matrix}CHMe\\CO\text{---}\end{matrix}>O,$$

melts at 212—213°. It does not dissolve in soda, and, when boiled with alcoholic solutions of the alkalis, yields salts of the hydroxy-acid. It is also formed by boiling ethylapocinchenic acid with lead peroxide and sulphuric acid. When reduced with amorphous phosphorus and hydriodic acid, it gives a quantitative yield of homapocinchene.

When boiled with hydrobromic acid, it yields the lactone of hydroxyapocinchenic acid, $C_9NH_6{\cdot}C_6H_3(OH)\langle{}^{CHMe}_{CO}\rangle O$, which melts at 274°. It is extremely stable towards oxidising agents. When converted into the alkali salt and treated with permanganate, it is slowly oxidised. When the alkali salt is treated with a solution of bromine in dilute sodium hydroxide, it yields quinolinephenetoïldicarboxylic acid.

Quinolinephenetoïldicarboxylic acid, $C_9NH_6{\cdot}C_6H_2(OEt)(COOH)_2$, melts at 230—240° with decomposition, gives unstable salts with mineral acids, and well-characterised metallic salts. The *anhydride* melts at 210—211°, and yields a fluoresceïn-like compound with resorcinol. When oxidised with chromic acid, it yields cinchoninic acid.

Ethylhomapocinchene, $C_9NH_6{\cdot}C_6H_3Et{\cdot}OEt$, when oxidised with lead peroxide or manganese dioxide and sulphuric acid, yields cinchoninic acid, ketoethylhomapocinchene and ethylhomapocinchenic acid.

Ketoethylhomapocinchene, $C_9NH_6{\cdot}C_6H_3(OEt){\cdot}COMe$, melts at 107—109°. The *phenylhydrazone* melts at 218—220°. When warmed with methyl alcohol, iodine, and potassium carbonate, it yields iodoform and ethylhomapocinchenic acid. The same acid is obtained by heating the ketone with an alkaline solution of bromine.

Ethylhomapocinchenic acid, $C_9NH_6{\cdot}C_6H_3(OEt){\cdot}COOH$, melts at 253—254°. When boiled with hydrobromic acid, it yields homapocinchenic acid, $C_9NH_6{\cdot}C_6H_3(OH){\cdot}COOH$, which does not melt at 290°.

Quinolinephenetoïl, $C_9NH_6{\cdot}C_6H_4{\cdot}OEt$, is obtained by heating the silver salt of the preceding acid at 280—290°, and melts at 80—81°. When boiled with concentrated hydrobromic acid, it yields *quinolinephenol*. The latter melts at 208°, and dissolves in fixed alkalis and mineral acids. The *hydrochloride* melts at 260°.

From the above results, the author deduces for apocinchene the formula $C_9NH_6{\cdot}C_6H_2Et_2{\cdot}OH$ [OH : Et : Et = 1 : 2 or 4 : 3].

E. C. R.

Constitution of Anhydroecgonine. By A. Einhorn and Y. Tahara (*Ber.*, **26**, 324—333).—In his paper on the constitution of tropine (Abstr., 1892, 360), Merlin has proposed for anhydroecgonine, which Einhorn had previously proved to be a tropidinecarboxylic acid, the constitutional formula $CH\langle{}^{CH_2\text{———}CH_2}_{CH{:}C(COOH)\text{—}CH}{}^{}_{CH_2\text{———}NMe}\rangle$; the further investigations described in the present paper bear out Merlin's supposition, except in the matter of the position of the carboxyl group, which, from the experiments now to be described, must be regarded as combined with one of the carbon atoms common to both the benzene and pyridine nuclei, the formula becoming

$$CH\langle{}^{CH_2\text{–}CH}_{CH\text{=}CH\text{—}C{\cdot}COOH}{}^{}_{CH_2{\cdot}NMe}\rangle.$$

The compound which forms the starting point of the authors' researches is the *methiodide* of *anhydroecgonine ethyl ether*, which is best prepared by the action of methylic iodide on an ethereal solution of the ethyl ether, and crystallises in white plates melting at 177°. The corresponding *methochloride* is obtained from it by the action of silver chloride, and forms a hygroscopic mass, which yields a crystalline *aurochloride* and *platinochloride*.

When the aqueous solution of the methiodide is carefully treated with silver oxide, it yields a new substance, which crystallises in colourless, apparently rhombic crystals, melts with decomposition at 169°, and yields an *aurochloride*, melting at 217°. The base has the composition $C_{10}H_{15}NO_2$, and consists of *paradimethyldihydrobenzylaminecarboxylic acid*, $NMe_2\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot CH\\CH:CH\end{matrix}>C\cdot COOH$; it is probable that the methohydroxide is first formed, and then loses alcohol. When boiled with aqueous soda, dimethylamine is evolved, and *paramethylenehydrobenzoic acid*, $CH_2:C<\begin{matrix}CH_2\cdot CH\\CH:CH\end{matrix}>C\cdot COOH$, remains in solution. This acid may also be obtained more directly by boiling the methiodide directly with soda solution and acidifying, and forms colourless, prismatic needles, melting at 33—34°; its *silver* salt crystallises in silky plates.

Methylenehydrobenzoic acid combines readily with bromine to form a *dibromide*, $C_8H_8O_2Br_2$, which crystallises from alcohol in slender needles, and melts with decomposition at 135°. When heated with a saturated solution of hydrogen bromide in acetic acid at 100°, it combines with 2 mols. HBr, yielding *paratoluic acid dihydrobromide*, which in all probability has the constitution

$$CMeBr<\begin{matrix}CH_2\cdot CH_2\\CH:CH\end{matrix}>CBr\cdot COOH.$$

It forms small, colourless crystals, melts with evolution of gas at 153°, and on boiling with aqueous soda and acidification, yields paratoluic acid, which was identified by its melting point and by conversion into the methyl ether and into terephthalic acid.

The formation of all these substances may be readily explained on the assumption that anhydroecgonine has the constitution assigned to it above; if this be correct, ecgonine itself must have one of the following formulæ: $CH<\begin{matrix}CH_2 — CH_2\\CH(OH)\cdot CH_2\\CH_2 — NMe\end{matrix}>C\cdot COOH$,

$CH<\begin{matrix}CH_2 — CH_2\\CH_2\cdot CH(OH)\\CH_2 — NMe\end{matrix}>C\cdot COOH$; as no γ-lactone has yet been obtained from ecgonine, the authors regard the second formula as the more probable.

When paradimethyldihydrobenzylaminecarboxylic acid is treated with hydrogen chloride in alcoholic solution, it is converted into the methochloride of anhydroecgonine ethyl ether; this change probably takes place in three stages, the ethylic salt of the acid being first formed, and then yielding a hydrogen chloride additive product

which undergoes an intramolecular change in which the pyridine nucleus is again formed, yielding an anhydroecgonine derivative.

H. G. C.

Alkaloïds of the Seeds of Lupinus albus. By A. SOLDIANI (*L'Orosi*, 1892, 325—348, and *Gazzetta*, **23**, i, 143—168; compare Abstr., 1892, 892).—The crystalline alkaloïd from the seeds of *Lupinus albus*, melting at 99°, is very soluble in alcohol, ether, or chloroform, less so in benzene and light petroleum; its hydrochloride with $2H_2O$ melts at 105—107°, not 124° as previously stated, and is very soluble in absolute alcohol. The hydriodide melts at 179—180°, but has, probably, not yet been obtained in a state of purity; it is sparingly soluble in cold alcohol or water. The platinochloride forms red crystals soluble in water and insoluble in absolute alcohol. The aurochloride is obtained in yellow crystals melting at 182—183°.

The hydrochloride of this alkaloïd is optically inactive, but the hydrochloride of the liquid isomeric alkaloïd accompanying it is dextrorotatory. On purification, the liquid alkaloïd may be obtained in beautiful, large crystals which are very deliquescent; the melting points of its derivatives seem to indicate its identity with lupanine from *Lupinus angustifolia*. The physiological action of the two hydrochlorides is at present under investigation. The injection of 0·005 gram of the inactive salt caused death in a frog of ordinary weight, whilst the same quantity of the active hydrochloride was not fatal.

W. J. P.

Proteïds of Egg White. By RAMSDEN (*Proc. physiol. Soc.*, 1892, 23—24).—A solution of white of egg, slightly acidified in the usual manner, and kept at a temperature considerably below that of the first coagulation as ordinarily determined (57·5°), nevertheless gives in time an abundant coagulum. Repeated crops of coagulum may be obtained on keeping a solution of white of egg at the lowest "coagulation temperature." The liquid is finally almost free from proteïd. A solution of Hofmeister's crystals of egg albumin, when investigated by the ordinary method of fractional heat coagulation, gives a series of coagula at temperatures almost identical with those at which coagula appear in solution of white of egg not previously freed from globulin. A solution of white of egg, freed from globulins by saturation with magnesium sulphate, gives a similar series of coagula. The ordinary method of fractional heat coagulation gives no certain indication of the presence or absence of the globulin.

W. D. H.

Behaviour of Proteïds towards concentrated Hydriodic acid. By N. v. LORENZ (*Zeit. physiol. Chem.*, **17**, 457—458).—In consequence of certain experiments by E. Meissl, in which he had used Zeisel's method of estimating methoxyl in connection with albuminous substances, it appeared necessary to determine, with pure proteïds, whether they contain the residue $O{\cdot}C_nH_{2n+1}$ (especially $O{\cdot}CH_3$), which is eliminated by hydriodic acid and is changed into the alkyl iodide. Distillation is carried on in a stream of carbonic anhydride with a solution in alcoholic silver nitrate, and the iodide is weighed

as silver iodide. The impure proteïds yielded silver iodide; the pure proteïds gave negative results. W. D. H.

Crystallised Vegetable Proteïds. By T. B. Osborne (*Amer. Chem. J.*, 662—689).—The author has recently, or on previous occasions, prepared crystallised globulins from Brazil nuts, hemp seed, castor oil beans, flax seed, oats, and squash seeds. He now describes their properties, and gives analyses of them, comparing these with analyses made by other investigators. These globulins are all obtained by extracting the powdered seeds (previously freed from husk by sifting, and from oil by extraction with ether or light petroleum) with a warm or cold solution of sodium chloride; the filtered extract, if warm, is allowed to cool, if cold, is subjected to dialysis, in order to remove the sodium chloride. In either case, the globulin separates out, either in crystals or in spheroïds, or as a mixture of both, that from hemp seed being most readily obtained crystalline. The crystals are always octahedra; sometimes they appear as hexagonal plates, but are then nothing but unequally-developed octahedra. The crystallised globulins of the Brazil nut (I) and of the oat (II) are distinct substances, for they react differently, and their composition is different, as the analyses show:—

	I.	II.	III.	IV.	V.	VI.
Carbon	52·18	52·18	51·28	51·31	51·66	51·48
Hydrogen ...	6·92	7·05	6·84	6·97	6·89	6·94
Nitrogen....	18·30	17·99	18·84	18·75	18·51	18·60
Sulphur.....	1·06	0·53	0·87	0·76	0·88	0·81
Oxygen.....	21·54	22·34	22·17	22·21	22·06	22·17
	100·00	100·00	100·00	100·00	100·00	100·00

On the other hand, the crystallised globulins of the hemp seed (III), castor oil bean (IV), squash seed (V), and flax seed (VI) are almost identical in composition, and behave in a very similar way towards reagents, those of hemp seed and castor oil beans being almost identical in the latter respect, although differing slightly from those of the squash and flax seed, which two likewise closely agree together. C. F. B.

Tunicin. By E. Winterstein (*Ber.*, **26**, 362—364).—Tunicin, purified by treatment with highly dilute acids and alkali, on hydrolysis with sulphuric acid, yields dextrose, which can be separated by means of alcohol and identified by its refractive power, the formation of the osazone and of saccharic acid, and by the action of yeast. J. B. T.

Organic Chemistry.

Influence of Negative Groups in Organic Compounds. By T. Selivanoff (*J. Russ. Chem. Soc.*, **24**, 134—135).—From his experiments on halogen amines and from other data, the author concludes that when a halogen atom is attached to a carbon atom which is directly combined with other strongly negative groups, it is possessed of "active" (that is, oxidising) properties. He adduces as instances, such compounds as $\cdot CX \cdot SO_2R$, $\cdot CX(SO_2R)_2$, where X is a halogen atom, and $CBr_2(NO_2)_2$, $CHBr(NO_2)_2$, $CMeBr(NO_2)_2$, and $CHMe_2 \cdot CBr(NO_2)_2$. J. W.

Composition of Commercial Amylene. By I. Kondakoff (*J. Russ. Chem. Soc.* **24**, 92—113).—Chlorine combines with the amylene prepared from methylpropylcarbinylic iodide, yielding an amylenic chloride (560 grams from 320 grams of amylene) boiling at 139·5—140·5°. A small quantity of a chloramylene is formed simultaneously. The amylenic chloride is identical with that produced by the addition of chlorine to symmetrical methylethylethylene. In this case, the quantity of chloramylene formed is exceedingly small. The sp. gr. of the chloride of methylethylethylene is 0·0973 at 0°/0° and 1·0821 at 20°/0°.

The author studied the action of chlorine on the hydrocarbons remaining after commercial amylene had been treated with concentrated sulphuric acid. 1000 grams yielded 405 grams of isopentane, and 1120 grams of different products containing chlorine, of which 720 grams boiled at 139—140·5°, and 280 grams at 142—144°. From the chief fraction, alcohols were obtained by prolonged treatment with water, and then with caustic potash. The alcoholic product was fractionated, and the separate fractions distilled with strong sulphuric acid. Amongst the products were found, methyl isopropyl ketone, methylpropylcarbinol, methylethylacetaldehyde, and isopropylacetaldehyde, but no normal valeraldehyde. From the velocity of etherification, it was shown that the mixture contained primary and secondary unsaturated alcohols, consisting, in fact, of β-dimethylallylic and α-ethylacrylic (or tiglic) alcohols, both derived from asymmetrical methylethylethylene.

The fraction of the chlorides boiling at 142—144° was shown to be the chloride of isopropylethylene.

The oxidation of the original mixture of hydrocarbons by potassium permanganate yielded acetaldehyde, propaldehyde, and isobutaldehyde, the corresponding acids, and also formic, oxalic, and dihydroxyvaleric acids. Neither normal butyric nor succinic acid could be detected.

From these observations, the author concludes that in commercial amylene there is no propylethylene, and that the product, after extraction with concentrated sulphuric acid, contains isopentane,

symmetrical methylethylethylene, and isopropylethylene, besides small quantities of trimethylethylene and asymmetrical methylethylethylene. J. W.

Syntheses in the Fatty Series by means of Zinc Chloride. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 309—317).—Trimethylethylene, if heated with zinc chloride at 70°, gives a considerable quantity of diamylene. The same hydrocarbon, when mixed with acetic acid and zinc chloride, at once forms an amylic acetate boiling at 124—135°. This, however, is a mixture of isomeric ethereal salts, and when treated with gaseous hydrogen chloride, yields tertiary amylic chloride and an ethereal salt boiling at 130—135°, probably $CH_3{\cdot}COO{\cdot}CH_2{\cdot}CHMeEt$, or $CH_3{\cdot}COO{\cdot}CHMePr^{\alpha}$.

When trimethylchloromethane is mixed in molecular proportion with trimethylethylene and a small quantity of zinc chloride, action takes place after some hours, and is complete in the course of a day. Diamylene is formed, possibly by the addition and subsequent withdrawal of hydrogen chloride. Acetic chloride acts at once on trimethylethylene under the influence of zinc chloride, giving an unsaturated ketone, $CMe_2{:}CMe{\cdot}CO{\cdot}CH_3$.

Isopropylethylene was not affected by remaining in contact with zinc chloride for eight months at the ordinary temperature.

The amylene obtained from the iodide of fermentation amyl alcohol gives a double compound with zinc chloride, which is decomposed by gaseous hydrogen chloride with formation of tertiary amylic chloride, and by water with formation of dimethylethylcarbinol. On prolonged contact, or rapidly at 100°, a diamylene is produced, and pure isopropylethylene remains behind unchanged.

J. W.

Ethereal Salts of Nitrous acid. By I. BEVAD (*J. Russ. Chem. Soc.*, **24**, 125—127).—By the action of silver nitrite on isopropylic iodide, the author obtained a substance boiling at 39—39·5° under a pressure of 752 mm. On treatment with fuming hydriodic acid and hydrogen sulphide solution, it was converted into isopropyl alcohol and nitric oxide. With alcoholic soda, it gave sodium nitrite and ethyl isopropyl ether. An alcoholic solution of sodium nitrite gives the precipitates with cupric sulphate, ferric chloride, and silver nitrate which have been supposed to characterise the nitro-compounds.

From these experiments, the author concludes that the substance is a true ethereal salt of nitrous acid, RO·NO. Similar results were obtained with the products from silver nitrite and ethylic and methylic iodides. J. W.

Action of Zinc Chloride on Fatty Alcohols. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, **24**, 114—123).—From a consideration of the results obtained by various observers, the author classifies the different actions of zinc chloride on fatty alcohols as follows:—

a. Dehydration with formation of simple ethers and olefines.

b. Isomerisation of these olefines.

c. Formation of homologues of the olefines which have the same number of carbon atoms as the alcohols employed.

d. Polymerisation of the olefines.

e. Reduction of the olefines.

f. Etherification of the alcohols.

g. Oxidation of the alcohols (to aldehydes).

He also discusses at some length the formation of the isomeric amylenes obtained from isoamyl alcohol by means of zinc chloride.

J. W.

Action of Iodine on Sodium Propoxide. By A. Kessler (*J. Russ. Chem. Soc.*, **24**, 299—304).—Sodium (16·5 grams) was dissolved in propyl alcohol (175 grams), and the solution cooled to 6°, when it solidified. Iodine (450 grams) was then added in small portions at a time with continual shaking. The reaction went on quietly, the alcoholate disappearing, and sodium iodide precipitating. Finally, the cooled solution was neutralised with a 10 per cent. solution of tartaric acid, and treated with enough water to precipitate the whole of the iodoform produced during the action. The aqueous liquid was then separated by distillation into fractions boiling at 89—92°, 92—100°, and 100—100·5°. Each of these was then carefully fractionated by itself. From the first portion, which consisted chiefly of a mixture of propyl alcohol and water of constant boiling point, an oil was obtained which distilled between 111° and 114° under a pressure of 26—28 mm., and, on analysis, gave numbers agreeing with the formula $C_9H_{20}O_3$. A molecular weight determination by the cryoscopic method confirmed this formula. From its behaviour towards acetic acid, on heating with which it gives propylic acetate, and what is apparently an hydroxyaldehyde, the author concludes that the substance is the dipropyl ether of α-hydroxypropaldehyde, OPr·CHMe·CH(OH)·OPr.

J. W.

Action of Sodium on Epichlorhydrin. By N. Kijner (*J. Russ. Chem. Soc.*, **24**, 31—39).—Hübner and Müller (*Annalen*, **159**, 184) found that sodium and epichlorhydrin reacted in ethereal solution with separation of sodium chloride and formation of the sodium compound of a substance b. p. 218—225°, to which they attributed the formula $C_6H_{12}O_2$. The author has repeated their experiments as follows:—Sodium (70 grams) in the granular form was covered by a layer of dry ether, and to it epichlorhydrin (100 grams) was added drop by drop, the flask being cooled with ice, and frequently shaken. A yellowish solid mass was formed, consisting of a mixture of sodium chloride and the sodium compound of an alcoholic product. After a lapse of 12 hours, the contents of the flask were treated with small quantities of dilute alcohol to destroy the excess of sodium, then with a large quantity of water, and were finally acidified with sulphuric acid. The ethereal layer was dried and the ether distilled off, when 36 grams of an oil free from chlorine remained behind; on fractionation, this yielded a small quantity of allyl alcohol, a product boiling at 225—227°, and a thick oily residue. The portion boiling at 225—227° was proved by

analysis and by the determination of the lowering of the freezing point of benzene, to have the composition $C_9H_{16}O_3$, not $C_6H_{12}O_2$, as found by Hübner and Müller. It united readily with bromine, and was reduced at 100° by hydriodic acid (sp. gr. 1·96) to isopropylic iodide. Acetic chloride gave a monacetate. From these reactions, it appeared probable that the substance was a diallyl ether of glycerol, formed by the action of sodium allyl oxide on epichlorhydrin. Experiment showed this explanation to be the correct one, allyl alcohol, sodium, and epichlorhydrin interacting very readily, with formation of a diallyl ether of glycerol. The author has not determined which of the possible isomerides is produced, nor, indeed, that the substance is not a mixture of both.

Diallyl ether of glycerol, $C_9H_{16}O_3$. B. p. 224—228°. Sp. gr. at 0°/0°, 0·997; at 18°/0°, 0·9824. *Acetate*, $C_9H_{15}O_3Ac$. B. p. 240—244°. Sp. gr. at 20°/0°, 1·000.

The diallyl ether seems to polymerise on keeping, becoming viscous, and giving a depression of the freezing point in benzene solution nearly corresponding with a molecule double that of the ether.

J. W.

Phlorose. By E. Schunck and L. Marchlewski (*Ber.*, **26**, 942—943).—The authors bring forward conclusive proof of the accuracy of Rennie's results (Trans., 1887, 636), that the so-called phlorose is identical with d.-glucose (dextrose). A. R. L.

Action of Hydrogen Peroxide on Starch. By A. v. Asbóth (*Chem. Zeit.*, **16**, 1517—1518; 1560—1561).—Lintner (Abstr., 1891, 537) has studied the action of potassium permanganate, and Petit (Abstr., 1892, 1171) that of nitric acid, on starch.

When a paste of potato starch (150 grams) and water (500 grams) is boiled during the addition of hydrogen peroxide (750 grams) made faintly alkaline with ammonia, liquefication sets in at the end of a minute, and oxygen and carbonic anhydride are evolved. The yellow solution is filtered from the precipitate, which is probably starch cellulose, and the filtrate fractionated as described below. The compounds obtained are without action on Fehling's solution, but reduce silver nitrate solution, forming metallic mirrors; on being boiled with hydrochloric acid, they are readily saccharified.

The first separation is effected by pouring the last mentioned filtrate into 96·5 per cent. alcohol (3 litres); the precipitate which represents the chief part of the transformation product is kneaded with alcohol; it forms a grey, porous mass; its aqueous solution gives a bluish-violet coloration with iodine, and its specific rotatory power is $[\alpha]_D = 178°$. It holds iron and copper salts in solution in the presence of alkalis, but is precipitated from its aqueous solution on the addition of either alcohol or barium hydroxide. Analysis gave values agreeing with the empirical formula $C_6H_{10}O_5 + H_2O$, and the author regards it as identical with "soluble starch" or "amylodextrin."

If the alcoholic filtrate is allowed to remain for a time, another substance, $C_{24}H_{42}O_{20} + 4H_2O$, separates, the aqueous solution of which gives a violet-red coloration with iodine. It is precipitated from its aqueous

solution by alcohol, but not by barium hydroxide, and its specific rotatory power is $[\alpha]_D = 170°$.

Barium hydroxide is added to the alcoholic filtrate from the last-described compound, and the resulting precipitate is dissolved in hydrochloric acid and the barium precipitated by sulphuric acid. When purified by dissolving it in water and reprecipitating with alcohol, it forms a pulverulent mass having the composition $C_6H_8O_4 + H_2O$. It gives no coloration with iodine.

The substance remaining in the alcoholic solution after the last separation consists of a small quantity of sugar. A. R. L.

Inulin, Pseudoinulin, and Inulenin. By C. Tanret (*Compt. rend.*, **116**, 514—517).—In the Jerusalem artichoke, and in elecampane, inulin is associated with two allied substances, *pseudoinulin* and *inulenin*. The three compounds are separated by means of their different solubilities in solutions of barium hydroxide.

The boiling juice of artichokes taken up in September or October is treated with lead acetate, and after cooling and separation of the lead by means of sulphuric acid, a concentrated solution of barium hydroxide is added so long as a precipitate forms, and then 20 per cent. of alcohol of 80°. The precipitate is washed with cold barium hydroxide solution, then decomposed by carbonic anhydride, and mixed with a large quantity of cold barium hydroxide solution. The precipitate obtained under these conditions is rich in inulin, but contains little of the other two compounds. The inulenin and pseudoinulin are in the mother liquor, which is mixed with successive quantities of dilute alcohol, the precipitates that form being collected and decomposed by carbonic anhydride.

The compound of inulin with baryta is repeatedly treated in the same manner until all pseudoinulin and inulenin have been removed, and it is then dissolved in hot water, decomposed by carbonic anhydride, the solution filtered, treated with animal charcoal, and mixed with alcohol of 95°. Pure inulin separates, and is washed with concentrated alcohol.

The solutions containing pseudoinulin and inulenin are evaporated to dryness, dissolved in a cold solution of pure barium hydroxide, and mixed with a further quantity of the same solution until the precipitate ceases to form. This precipitate, when decomposed by carbonic anhydride, yields pseudoinulin.

The solution is treated with carbonic anhydride, filtered, and evaporated to dryness. The residue is agitated with 10 times its weight of water, filtered after 24 hours, evaporated to dryness, and the residue treated with five or six times its weight of boiling alcohol of 30°, from which the inulenin crystallises.

Inulin deposited from water or dilute alcohol forms compact, transparent masses when dried, but if previously washed with strong alcohol, it forms a pulverulent solid resembling starch. After drying at 100°, its rotatory power is $[\alpha]_D = -38{\cdot}8°$, and is not affected by the temperature or concentration of the solution. Its composition agrees with Kiliani's formula, $6C_6H_{10}O_5,H_2O$, but cryometric observations indicate that this must be quintupled to represent the molecule.

With barium hydroxide, inulin forms the compound $C_{36}H_{62}O_{31},3BaO$. Inulin dissolves in 10,000 parts of cold water, but is readily soluble in hot water, and also in hot dilute alcohol; contrary to the usual statement, its solutions are not opalescent.

. *Pseudoinulin*, according to analysis and cryometric observations, has the composition $16(C_6H_{10}O_5),H_2O$. With baryta in aqueous solution, it forms the compound $16(C_6H_{10}O_5),H_2O,6BaO$, but in presence of alcohol the compound formed is $16(C_6H_{10}O_5),H_2O,8BaO$. The calcium compound formed in presence of alcohol is analogous in composition. Basic lead acetate does not precipitate pseudoinulin, but in presence of ammonia the compound $16(C_6H_{10}O_5),H_2O,19PbO$ is formed. Pseudoinulin resembles inulin in appearance, but dissolves in 350 to 400 parts of cold water, and is very soluble in hot water and in hot dilute alcohol. Its rotatory power is $[\alpha]_D = -32{\cdot}2°$, and when treated with dilute acids it becomes $[\alpha]_D = -85{\cdot}6°$. The mixture of sugars obtained by inversion very readily yields crystallised levulose, and also contains a dextrogyrate sugar which is probably glucose.

Inulenin when dried at 100° has the composition $10(C_6H_{10}O_5),2H_2O$. It crystallises in slender needles, macled in pairs or arranged in stellate groups; they act on polarised light and show extinction parallel with their axes. Inulenin dried at 100° dissolves in a few parts of cold water, then becomes hydrated, and crystallises, the liquid retaining only about one-eighth of its weight of the compound. It dissolves in 35 parts of cold alcohol of 30°, and in 245 parts of alcohol of 50°. Its rotatory power is $[\alpha]_D = -29{\cdot}6°$, but after inversion it becomes $[\alpha]_D = -83{\cdot}6°$. With barium, calcium, and lead oxides, inulenin forms compounds analogous to those of inulin and pseudoinulin. C. H. B.

Glycogen. By S. Fränkel (*Pflüger's Archiv*, **52**, 125—136).—A method for the preparation of glycogen in the cold is recommended, by means of which the conversion of glycogen into sugar is prevented as efficaciously as by heat. It consists in the use of dilute acids as the agents for extracting it from liver and muscle. Several acids were used, but the best results were obtained with a 2—4 per cent. solution of trichloracetic acid. No proteïd goes into solution. The glycogen is precipitated by alcohol. It gives the usual reactions of glycogen; elementary analysis gives the formula $6C_6H_{10}O_5 + H_2O$, $[\alpha]_D = 197{\cdot}891°$; this is a smaller value than is given by most previous observers. Doubt is expressed as to whether glycogen occurs in the body as such; water will not extract it from liver which has been hardened in alcohol; the same is true for mixtures of glycogen and albumin which have been treated with alcohol. Boiling water and the addition of small quantities of salts of the heavy metals and acids will, however, extract the glycogen.

It is regarded as probable that in the living cells a complex compound of proteïd and carbohydrate exists, which may be split up by metabolic processes, or by various reagents, the carbohydrate being separated under some circumstances as glycogen, under others as sugar. W. D. H.

Witt's Oxycellulose. By A. NASTNIKOFF (*J. Russ. Chem. Soc.*, **24**, 256—275).—The author, from experiments on the action of bleaching powder solutions on Schleicher and Schüll's filter paper, finds that no oxycellulose is formed at 19—20° if the bleaching powder solution contains less than 9·86 grams of active chlorine per litre.

The oxycellulose he obtained is turned brown by iodine, and dissolves completely in Schweitzer's reagent, from which it is again precipitated by acids. It also dissolves without residue in Cross and Bevan's solvent (zinc chloride in concentrated hydrochloric acid), the saturated solution containing about 1 gram of oxycellulose in 100 c.c. Dilution of this solution with its own volume of water brings down all the precipitate that will fall out under the circumstances. Acid sodium sulphite has no action on oxycellulose, either at the ordinary temperature or at 100°; at 140° the oxycellulose is completely destroyed. The action of moist chlorine produces no substance which gives a coloration with neutral sodium sulphite, so that if oxycellulose is, as Witt maintains, an intermediate stage between cellulose and lignin, it is much nearer the former than the latter.

The author made a large number of analyses of oxycellulose, prepared under different conditions, and comes to the conclusion that it is not a homogeneous substance. Judging from the action of phenylhydrazine, oxycellulose cannot contain more than 15 per cent. of $C_6H_{10}O_6$, supposing this to possess a carbonyl group capable of condensing with the reagent. J. W.

Absorption of Mercuric Chloride from Dilute Solutions by Cotton. By L. VIGNON (*Compt. rend.*, **116**, 517—519 and 645—646).—Carefully purified cotton, bleached by dilute bleaching powder solution and thoroughly washed, absorbs mercury from dilute solutions of mercuric chloride, leaving the solution relatively richer in chlorine.

Part of the mercuric chloride absorbed by cotton wool is soluble in cold water, and is present in the form of unchanged mercuric salt; part is soluble in hydrochloric acid and is present as mercuric oxide, and the remainder is soluble in concentrated sodium chloride solution, and is present as mercurous chloride. At the ordinary temperature, the mercury compounds absorbed consist of 22 to 28 per cent. of mercuric chloride, 59 to 70 per cent. of the oxide, and 8 to 13 per cent. of mercurous chloride. If the cotton, after immersion, is kept for 20 days at the ordinary temperature, and then heated at 60° for 10 hours, it contains 12 to 22 per cent. of mercuric chloride, 25 to 57 per cent. of the oxide, and 22 to 53 per cent. of mercurous chloride. It is probable that the mercurous chloride is formed by the interaction of mercuric chloride and mercuric oxide, thus: $HgCl_2 + HgO = Hg_2Cl_2 + O$, the oxygen combining with the cellulose to form oxycellulose. C. H. B.

Dimorphism of Dimethylamine Platinochloride. By LE BEL (*Compt. rend.*, **116**, 513—514).—When a solution containing di-

methylamine and diisobutylamine platinochlorides is allowed to crystallise, no double platinochloride is formed, but the dimethylamine platinochloride separates in the form of yellowish, rhombic needles with a characteristic angle of 48° 20′, quite different in appearance from the ordinary crystals. This dimorphic form was described by Vincent, but the conditions under which it is produced were not determined. It is this form, and not the ordinary form, of the salt that resembles the rhombic crystals of the platinochlorides of the other diamines.

The sp. gr. of the ordinary crystals is 2·27, that of the rhombic crystals 2·12. The rhombic crystals, as Vincent observed, are stable at 100° when dry, but they reproduce the ordinary form on recrystallisation. A certain number of the rhombic crystals are, however, always found, even when the salt has been dissolved in hot water, and hence it would seem that the crystalline type is conserved even in solution. This view is confirmed by the fact that the rhombic crystals are obtained by keeping a pure solution of the dimethylamine platinochloride below 0° for some time. It would seem that 10° is the critical temperature, above which there is a tendency to return to the ordinary form. At the same time, a solution that has been exposed to a low temperature for a long time, and is then heated at 30°, yields rhombic crystals during the first eight days, and afterwards the ordinary crystals. The rhombic form can be reproduced by adding cubic crystals of trimethylamine platinochloride, and, although the change is slow, the crystals obtained are large, and it is observed that the change of form is preceded by the formation of macles.

C. H. B.

Haloïd Substitution Products of Amides. By T. Selivanoff (*J. Russ. Chem. Soc.*, **24**, 132—134; compare this vol., i, 192 and 305).—The author regards the halogen substitution products of ammonia and the amides as being amides of hypochlorous, hypobromous, and hypoiodous acids, for in presence of water they give the reactions of these acids. For each atom of chlorine in a chloramido-compound 2 atoms of iodine are liberated from a solution of potassium iodide on acidification.

By making use of the following reaction between amines and haloïd substituted amides, $RNH_2 + 2CH_3{\cdot}CO{\cdot}NHBr = RNBr_2 + 2CH_3{\cdot}CO{\cdot}NH_2$, the author has succeeded in preparing a whole series of bromamines, &c.

Acetiodamide, $CH_3{\cdot}CO{\cdot}NHI$, was prepared by the action of iodine on the mercury or silver compound of acetamide. It is easily decomposed by water, giving hypoiodous acid, HIO, which is unstable, being at once converted into iodine and iodic acid according to the equation $5HIO = 2I_2 + HIO_3 + 2H_2O$. A similar decomposition was observed in the case of succiniodimide, $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NI$.

It has been stated that chloride of nitrogen is decomposed by water into nitrous acid and hydrochloric acid, but the author finds that this is not the case, hypochlorous acid being the product of the reaction.

J. W.

Nitrosoguanidine. By J. THIELE (*Annalen*, **273**, 133—144).—*Nitrosoguanidine*, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}NO$, is formed as an intermediate product in the reduction of nitroguanidine to amidoguanidine (Abstr., 1892, 1295); on carefully treating the nitro-compound with zinc-dust and sulphuric acid and recrystallising the product from hot water, nitrosoguanidine is deposited in slender, yellow needles. It explodes rather violently at 160—165°, and is insoluble in alcohol, but dissolves in alkalis, being reprecipitated from the solution by carbonic acid; it is readily soluble in dilute mineral acids, the solutions undergoing decomposition, even at the ordinary temperature, with evolution of nitrous acid and formation of guanidine. It gives Liebermann's reaction, and decomposes suddenly when treated with concentrated sulphuric acid; its alkaline solutions give, with ferric salts, a beautiful, purple coloration which disappears when the solution is exposed to the air or treated with oxidising agents. When boiled with water, it is decomposed into nitrogen, cyanamide, and water; on oxidation, it gives nitroguanidine, and, on reduction, amidoguanidine. The *hydrochloride*, CH_4N_4O,HCl, is a yellow powder, readily soluble in alcohol; it is decomposed by water, and is extremely unstable in the dry state, exploding sometimes at ordinary temperatures. The *silver* derivative, CH_3N_4OAg, is a colourless, flocculent, explosive substance, and is readily soluble in acids. The *copper* derivative, $(CH_3N_4O)_2Cu$, is a reddish-brown, the *nickel* derivative, $(CH_3N_4O)_2Ni$, a vermilion substance.

When nitrosoguanidine is treated with an equivalent quantity of hydrazine hydrate, it is converted into amidoguanidine with evolution of nitrogen; when, however, 2 molecular proportions of the nitroso-compound are employed to 1 of the hydrate, hydrazodicarbonamidine (*loc. cit.*) is formed. F. S. K.

Formaldehyde. By G. PULVERMACHER (*Ber.*, **26**, 955—958).—Methylenediorthonitraniline (Abstr., 1892, 1450) is readily prepared by adding a solution of formaldehyde to one of orthonitraniline in boiling 5—10 per cent. alcohol. On reduction, the three isomerides (*loc. cit.*) yield the corresponding phenylenediamines.

Methylenephthalamic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}N{:}CH_2$, is obtained by heating together phthalamide and formaldehyde in a sealed tube at 100°; it crystallises in prisms, melts at 144°, is almost insoluble in water, and is hydrolysed into formaldehyde and phthalamide when boiled with that liquid. The *silver* salt is a white powder, which is not altered by exposure to light. When a mixture of formaldehyde and oxamide is heated at 130°, ammonium oxalate is formed.

A. R. L.

Condensation of Chloral with Ketones. By J. WISLICENUS, T. KIRCHEISEN, and E. SATTLER (*Ber.*, **26**, 908—915).—The authors have unknowingly been working in the same direction as Koenigs (Abstr., 1892, 694; and this vol., i, 302).

When a mixture of chloral and acetone is heated in a sealed tube at 100°, and then at 150°, a mixture of trichlorethylideneacetone, $CCl_3{\cdot}CH{:}CH{\cdot}COMe$, and chloralacetone, $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$, is

obtained. The former is separated by distillation with steam; it boils at 136—140° under 120 mm. pressure.

Chloralacetone has the properties assigned to it by Koenigs. The oxime crystallises in beautiful, radiating needles, and melts at 104—106° (Koenigs gives m. p. 95—105°). When the lactone is warmed with sodium hydroxide or carbonate, large quantities of resin are formed, together with formic and acetic acids, and a crystalline acid, which the authors believe to be β-acetylacrylic acid. *Dibromochloralacetone* crystallises in colourless, silky needles, and melts at 117—118°.

Chloralacetophenone has the properties assigned to it by Koenigs. It melts at 76°. The oxime melts at 131—132°. The hydrazone melts at 141—142°. When treated with bromine in carbon bisulphide solution, it yields one monobromo-derivative, and not two as stated by Koenigs, who used chloroform as the solvent; this crystallises in colourless, lustrous prisms, and melts at 97°.

Trichlorethylideneacetophenone is most easily obtained by warming chloralacetophenone with phosphoric anhydride. It crystallises from alcohol in leaflets, from carbon bisulphide in thin, rhombic tablets, and from light petroleum in glassy prisms, and melts at 100°. By prolonged treatment at the ordinary temperature with water acidified with hydrochloric acid, and more quickly at 140°, it is converted into chloralacetophenone. The *oxime* crystallises from nitrobenzene in white needles, and melts at 300° with decomposition. The *dibromoderivative*, CCl_3·CHBr·CHBr·COPh, crystallises in tablets, and melts at 65—66°.

When chloralacetophenone is mixed with sodium carbonate and the mixture subjected to steam distillation, it yields chloroform, acetophenone, benzoic acid, formic acid, and a non-volatile acid, which the authors believe to be *diphenacylacetic acid*, $COOH·CH(CH_2·CPhO)_2$. The latter crystallises in silky needles, and melts at 131—132°.

The following salts are described: *Sodium* salt, *calcium* salt, $C_{36}H_{30}O_8Ca + 6H_2O$; *barium* salt, $C_{36}H_{30}O_8Ba + 6H_2O$; *silver* salt, $C_{18}H_{15}O_4Ag$. The *ethylic* salt crystallises in long, silky needles, and melts at 64°. E. C. R.

Pinacone from Ethyl Methyl Ketone. By N. Zelinsky and S. Krapivin (*J. Russ. Chem. Soc.*, **24**, 24—26).—Ethyl methyl ketone was prepared from diethylic methylacetoacetate, and reduced according to the directions given by Lavrinovitch (*J. Russ. Chem. Soc.*, **7**, 235; **8**, 338). In this way an oil was obtained, which was distilled, and collected in three fractions, namely, below 200°, at 200—205°, and at 205—210°. The first fraction was liquid, the second and third partially solid. After remaining for a long time in a desiccator, the solid was separated from the oily liquid and recrystallised from ether. It then melted at 49·5°, and had the composition of the pinacone, OH·CMeEt·CMeEt·OH. The oil in the fraction 200—205° had the same composition. There are, probably, therefore two geometrically isomeric pinacones formed by the reduction, the formula given above containing two similar asymmetric carbon atoms. J. W.

Action of Potassium Carbonate on Dichloroketones. By A. E. Favorsky (*J. Russ. Chem. Soc.*, **24**, 254—255).—The dichloroketone, $CH_2Me{\cdot}CCl_2{\cdot}COMe$, obtained by the addition of hypochlorous acid to methylethylacetylene, was heated with a 10 per cent. solution of potassium carbonate. Amongst the products of the reaction the following substances were found. The tetramethylquinone of Nef and Pechmann, which crystallised in characteristic, yellow needles and melted at 111°; a liquid acid boiling at 181—183°, the calcium salt of which gave on analysis numbers corresponding with the formula $Ca(C_5H_7O_2)_2$; and a solid acid melting at 45°, probably angelic acid. The author conceives the reaction to take place as follows: First, the dichloroketone is converted by the carbonate into a diketone, which under the influence of the alkali is converted, on the one hand, into tetramethylquinone, and, on the other, combines with a molecule of water, and, like benzile, undergoes isomeric transformation into a hydroxy-acid, in this case methylethylglycollic; the latter, under the conditions of its formation, at once splits up into water and two unsaturated acids—angelic and ethylacrylic. J. W.

Action of Iodine on the Silver Salts of Fatty Acids. By A. Simonini (*Monatsh.*, **14**, 81—92).—The author has previously shown (compare Abstr., 1892, 1301) that, by the action of iodine on the silver salts of acetic and caproic acids, at a temperature slightly above 100°, methylic acetate and amylic caproate, respectively, are formed. He has recently extended his investigations to the silver salts of butyric and palmitic acids, which under similar conditions, yield propylic butyrate and pentadecylic palmitate respectively, and finds that the reaction takes place in two phases. At the ordinary temperature silver iodide separates, but the alkylic salts named above are not formed until a temperature of about 100° is reached.

When a mixture of iodine and silver caproate is heated to a temperature slightly below 50°, and the product is exhausted with light petroleum, a peculiar compound, which contains iodine, silver, and the acid radicle, is obtained. It is very unstable, and is readily decomposed by water, giving silver iodide (2 mols.), silver iodate (1 mol.), and the free acid (6 mols.), and, therefore, resembles the salts of hypoiodous acid, which are not known in the free state, but appear to be decomposed by water, forming 2 mols. of iodide to each mol. of iodate. It, consequently, is best represented by the formula $C_5H_{11}{\cdot}COO{\cdot}I'''(OAg){\cdot}CO{\cdot}C_5H_{11}$. The formula explains its resolution, on heating, into amylic caproate, carbonic anhydride, and silver iodide, and the fact that, when reduced in petroleum solution with ordinary phosphorus, it gives a mixture of silver iodide and the anhydride of the acid. G. T. M.

Oximidoacetic acid. By P. P. Rubtzoff (*J. Russ. Chem. Soc.*, **24**, 247—248).—Potassium glyoxylate (1 mol.), hydroxylamine hydrochloride (1·5 mol.), and potassium hydroxide (1·25 mol.) are dissolved in water, and the aqueous solution allowed to remain for a long time at the ordinary temperature; on subsequent acidification

with hydrochloric acid and frequent extraction with ether, a white, crystalline mass is obtained soluble in water, and melting at 127—130°. On fusion, however, it decomposes with evolution of hydrocyanic acid. On analysis, numbers were obtained agreeing approximately with the formula $C_2H_3NO_3$, the substance being in all probability oximidoacetic acid, NOH:CH·COOH. The yield was 21 per cent. of that theoretically possible. A larger proportion may be obtained by using dibrom- or dichlor-acetic acid and excess of potash instead of glyoxylic acid. J. W.

Amides of Hypoiodous acid. By T. Selivanoff (*Ber.*, **26**, 985—989).—Iodyl succinimide, $C_2H_4<^{CO}_{CO}>NI$, was prepared by the author by acting on mercury succinimide with iodine in pure dry ethylic acetate. The solution in water has bleaching properties, iodises acetanilide, liberates iodine from potassium iodide solution and oxygen from barium peroxide. It behaves, in fact, potentially as a solution of succinimide and hypoiodous acid. If a large excess of succinimide is added, the solution becomes much more stable and can be boiled without undergoing decomposition.

Iodyl acetamide, $CH_3·CO·NHI$, is much less stable than iodyl succinimide, but a colourless, aqueous solution of it may be obtained. J. W.

Presence of Linoleïc acid in some Animal Fats. By D. Kurbatoff (*J. Russ. Chem. Soc.*, **24**, 26—31).—From the increase in weight of certain animal fats by oxidation in the air, the author suspected the presence in them of an acid less saturated than oleïc acid. He therefore subjected to oxidation the acids obtained from these fats by means of potassium permanganate in alkaline solution, and investigated the hydroxy-acids produced. From 29 grams of acid from the fat of the white hare he obtained 10 grams of dihydroxystearic acid (m. p. 130—134°) and 1 gram of an acid soluble in boiling water, and melting at 157—161°. From an investigation of its salts, this acid proved to be a monobasic acid having the composition $C_{18}H_{36}O_4$, being, in fact, a tetrahydroxystearic acid formed from an acid $C_{18}H_{32}O_2$ (probably linoleïc acid) present in the original substance. The same tetrahydroxy-acid was obtained from the fat of the grey hare, the Caspian seal, the silurus, and the sturgeon, although in only very small quantity from the fish. J. W.

Propylideneacetic acid and Ethylidenepropionic acid. By A. Viefhaus (*Ber.*, **26**, 915—922).—A mixture of propylideneacetic acid and ethylidenepropionic acid is obtained by heating a mixture of malonic acid, propaldehyde, and acetic acid on the water-bath. According to Ott (Abstr., 1891, 1453), the barium salt obtained from this mixture, which is crystalline and sparingly soluble in alcohol, is barium propylideneacetate, whilst the amorphous soluble salt is barium ethylidenepropionate. The author arrives at exactly the opposite conclusion.

The two acids were separated as described by Ott. The acid obtained from the crystalline barium salt boils at 120—121° under

62·5 mm. pressure, and when oxidised with potassium permanganate or nitric acid, yields oxalic and acetic acids. It is, therefore, ethylideneпropionic acid.

The acid from the amorphous barium salt boils at 126—127° under 62·5 mm. pressure, and on oxidation yields oxalic and propionic acids, and is therefore propylideneacetic acid.

Both acids, when boiled in a reflux apparatus with sulphuric acid, diluted with an equal volume of water, yield valerolactone. Ethylideneпropionic acid is, however, more easily converted into the lactone than propylideneacetic acid. E. C. R.

Action of Sulphuric acid on Behenolic acid. By A. Holt and J. Baruch (*Ber.*, **26**, 838—842).—When behenolic acid is dissolved in concentrated sulphuric acid, it becomes oxidised to *oxybrassidic acid*, $O<\begin{matrix}C\cdot C_{19}H_{39}\\ \|\\ C\cdot COOH\end{matrix}$, which crystallises in white plates melting at 83°, and yields a white *silver salt*, $C_{22}H_{39}O_3Ag$, stable in light. Treated with gaseous hydrogen chloride in alcoholic solution, this acid yields *ethylic dihydroxybrassidate*, $C_{19}H_{39}\cdot C(OH):C(OH)\cdot COOEt$, which forms colourless plates melting at 54°, and, like oxybrassidic acid, does not take up bromine, and yields no acetyl or benzoyl derivative. With phenylhydrazine at 150°, oxybrassidic acid yields a *phenylhydrazide*, $C_{21}H_{39}O\cdot CON_2H_2Ph$, melting at 111°, and with hydroxylamine in alcoholic soda, an *oxime*, $NOH:C_{21}H_{39}\cdot COOH$, melting at 44—45°, the *ethylic salt* of which, $NOH:C_{21}H_{39}\cdot COOEt$, melts at 28—29°. When warmed with strong sulphuric acid, this oxime is transformed into an isomeric substance, $C_{21}H_{40}NO\cdot COOH$, melting at 84—85°; the *ethylic salt*, $C_{21}H_{40}NO\cdot COOEt$, melts at 54°. C. F. B.

Action of Methylenic Iodide on Ethylic Acetoacetate. By C. T. L. Hagemann (*Ber.*, **26**, 876—890).—When methylenic iodide is heated with an alcoholic solution of ethylic sodacetoacetate, it combines with it to form a colourless oil, which has the composition $C_{10}H_{14}O_3$; this is, however, a mixture of two isomerides, which may be separated by treating the ethereal solution with aqueous soda, which dissolves one of the compounds. The soluble oil boils at 150—152° under 22 mm. pressure, and gives a red coloration with ferric chloride, whilst the insoluble oil boils at 148—152° under the same pressure, and gives no coloration with ferric chloride.

The first product of the reaction is, in all probability, ethylic diacetylglutarate, $CH_2[CH(COOEt)\cdot COMe]_2$; in presence of sodium ethoxide, the methyl group and the carbonyl group at the opposite end of the chain act on one another with elimination of water and formation of the compound $CH<\begin{matrix}CMe\cdot CH(COOEt)\\ CO—CH(COOEt)\end{matrix}>CH_2$; the latter then undergoes partial hydrolysis with simultaneous evolution of carbonic anhydride, yielding, according as one or other of the COOEt groups is eliminated, the two isomeric substances $C_{10}H_{14}O_3$, which have the following constitutional formulæ:—

$$CH<\begin{matrix}CMe\text{———}CH_2\\ CO\cdot CH(COOEt\end{matrix}>CH_2, \qquad CH<\begin{matrix}CMe\cdot CH(COOEt)\\ CO\text{———}CH_2\end{matrix}>CH_2.$$

As the compound soluble in alkali gives the colour reaction with ferric chloride characteristic of β-ketonic ethers, it has probably the first of the above formulæ.

By careful hydrolysis, both of the ethylic salts may be converted into the corresponding acids, which are extremely unstable, losing carbonic anhydride very readily, and could not therefore be closely examined. Both ethylic salts, when boiled with dilute sulphuric acid, lose the second COOEt group, forming one and the same compound, $C_7H_{10}O$, which is a mobile liquid having a pleasant characteristic odour; it boils at 200—201° (corr.), has a sp. gr. of 0·9714 at 20°/4°, and is soluble in water and the usual organic solvents. If the suppositions given above are correct, it must be 3-*methyl*-Δ_2-*ketohexenylene*, $CH\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}CMe\cdot CH_2\\ CO-CH_2\end{matrix}\begin{matrix}>\\ \\ \end{matrix}CH_2$. This is confirmed by the fact that it unites with sodium hydrogen sulphite, phenylhydrazine, and hydroxylamine, the *oxime*, C_7H_{10}·NOH, forming lustrous prisms, and melting at 158—159°, and that on oxidation with alkaline permanganate it yields γ-acetobutyric acid; chromic acid converts it into acetic and succinic acids and a substance which is possibly toluquinone.

The above reactions might also be explained if the substance $C_7H_{10}O$ had the constitution $COMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot C{:}CH$, which would be obtained if, in the formation of the anhydrides from ethylic diacetylglutarate, the methyl group had reacted with the carbonyl group adjacent to it; such a compound would, however, show the properties of an acetylene derivative, which is not the case with the substances above described. H. G. C.

Electrolytic Synthesis of Bibasic Acids. Part II. By A. Crum Brown and J. Walker (*Annalen*, **274**, 41—71; also *Trans. Roy. Soc. Edin.*, **37**, 361—379; compare Abstr., 1891, 1192, 1193).—After describing the electrolytic formation of the diethylic salts of the isomeric dimethylsuccinic and diethylsuccinic acids (Abstr., 1891, 1193), the authors proceed to the preparation and electrolysis of ethylic potassium dimethylmalonate. This salt is much more difficult to prepare than those already dealt with, which may all be obtained directly by half-saponification of the corresponding diethylic salt. Under the same conditions, diethylic dimethylmalonate is converted by the calculated quantity of alcoholic potash into a mixture of dipotassic dimethylmalonate and unchanged diethylic salt. By working at 0°, however, and using very dilute alcoholic solutions, 8 grams of potash being contained together with the methylic salt in 1750 c.c. of 95 per cent. alcohol, the ethylic potassium salt may be produced.

On electrolysis, an oil was obtained about two-thirds of which distilled above 200°, the greater part boiling between 240° and 250°; this fraction, when hydrolysed with hydrobromic acid (sp. gr. 1·7), yielded *tetramethylsuccinic acid*, m. p. 195°. The anhydride melted at 147—148°, and the dissociation constant of the acid was found to be $K = 0·0311$.

Ethylic potassium diethylmalonate was prepared in the same way as the corresponding salt of dimethylmalonic acid, and, on electro-

lysis, yielded an oil which boiled for the most part below 230°. The residue was fractionated at 12 mm. and gave a fraction boiling constant at 170°. This liquid was not diethylic tetrethylsuccinate, as might have been expected, but had the composition $C_{14}H_{26}O_4$. It was neutral, scarcely attacked by alcoholic potash, and had the sp. gr. 1·0082 at 13·5°/4°. A solid substance was obtained from it by heating at 110° with fuming hydrobromic acid. This was also neutral, and not appreciably attacked by any of the ordinary hydrolysing agents. It crystallised in longish, monosymmetric prisms ($a : b : c = 0·8811 : 1 : 0·9084$; $\beta = 84° 27'$), melting at 84·5°, and soluble in ether, alcohol, and benzene, insoluble in water, sparingly soluble in cold light petroleum, but fairly soluble in the hot solvent.

Together with the synthetical ethereal salts produced by the electrolysis of ethylic potassium salts, there are always formed larger or smaller quantities of oils of lower boiling point; these consist chiefly of the ethylic salts of unsaturated monobasic acids. Their formation occurs according to the equation

$$2COOEt\cdot R''\cdot CH_2\cdot CH_2\cdot COO\cdot = COOEt\cdot R''\cdot CH{:}CH_2 + COOEt\cdot R''\cdot CH_2\cdot CH_2\cdot COOH + CO_2.$$

Thus ethylic methylacrylate is produced from ethylic potassium dimethylmalonate, and ethylic ethylcrotonate from the corresponding diethylmalonate. The formation of unsaturated ethereal salts takes place much more readily with branched than with normal bibasic acids.

Ethylic potassium sebate, besides yielding the diethylic salt of *n*-dicarbodecahexanic acid, gives small quantities of the ethylic salt of an unsaturated acid, $C_9H_{16}O_2$, which has the formula

$$COOH\cdot[CH_2]_6\cdot CH{:}CH_2.$$

During the electrolysis, comparatively large quantities of diethylic sebate are regenerated.

The authors find that no synthetical product is obtained when the potassium ethylic salts of bromo-, hydroxy-, unsaturated, or aromatic acids are submitted to electrolysis. In their case, complete destruction of the molecule usually takes place at the anode. Potassium ethylic oxalate (prepared by boiling potassium acetate and diethylic oxalate in molecular proportions with ethyl alcohol, and filtering when cold) yields at the anode only carbonic anhydride and ethylene. Potassium methylic oxalate gives nearly pure carbonic anhydride.

J. W.

Decomposition of Solutions of Oxalic acid. By T. Gigli (*Chem. Centr.*, 1893, i, 11; from *Apoth. Zeit.*, **7**, 583—584).—The author draws the following conclusions from his experiments:—(1.) The decomposition of aqueous solutions of oxalic acid is caused by fungi or by direct exposure to light. (2.) Diffused light is most favourable to the growth of moulds. (3.) The most rapid decomposition is caused by the direct action of light. (4.) It seems probable that a decomposing action cannot be ascribed to oxygen. (5.) The carbonic anhydride that must be supposed to be formed is probably used up by the fungi, or, in decomposition by direct sunlight, is lost by diffusion; possibly, however, the decomposition of the

oxalic acid may be a reduction in which the products are carbonic oxide, oxygen, and water. A. J. G.

Derivatives of β-Methyladipic acid. By F. W. Semmler (*Ber.*, **26**, 774—776; compare this vol., i, 129).—*β-Methyladipic chloride*, $COCl\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot COCl$, is prepared by the action of phosphoric chloride on β-methyladipic acid, and boils without decomposition at 117—119° under a pressure of 10 mm.; its sp. gr. is 1·2201 at 20°, $n_D = 1·4709$, the molecular refractive power = 45·08. The *amide*, $C_7H_{10}O_2(NH_2)_2$, is deposited from water in colourless crystals which melt at 191°. Like the chloride, the amide is dextrogyrate.

The preparation of β-methylpentamethylenol, $\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2—CH_2\end{matrix}\!\!>\!CH\cdot OH$, from the corresponding amine by means of the diazo-reaction has been previously described (*loc. cit.*); it is more readily obtained by the reduction of β-methylketopentamethylene in alcoholic solution by means of sodium; its sp. gr. is 0·9169 at 20°, $n_D = 1·4521$, molecular refractive power = 29·40.

By varying the experimental conditions slightly, the ketone also yields an oily reduction product, which boils at about 244° and appears to be a pinacoline.

On heating β-methylpentamethylenol at about 120° with its own weight of zinc chloride, *α-methylpentamethylenylene*, $\begin{matrix}CHMe\cdot CH\\ |\\ CH_2—CH_2\end{matrix}\!\!>\!CH$, is formed; it is a colourless oil with an odour like that of allylic sulphide, and boils at 69—71° under the ordinary atmospheric pressure; its sp. gr. is 0·7851 at 20°, $n_D = 1·4201$, molecular refractive power = 26·91. The hydrocarbon is dextrogyrate, and its constitution is proved by the fact that, on oxidation with potassium permanganate, it yields α-methylglutaric acid. J. B. T.

Condensation of Cyanides with Ethereal Salts by means of Sodium Ethoxide. By H. Fleischhauer (*J. pr. Chem.* [2], **47**, 375—393; compare Abstr., 1892, 431).—*Ethylic sodiocyanopyruvate*, $CN\cdot CHNa\cdot CO\cdot COOEt$, is a crystalline mass obtained by the action of sodium ethoxide on methylic cyanide and ethylic oxalate. The *silver* derivative was analysed, but attempts to isolate ethylic cyanopyruvate failed. The *oxime* and *hydrazone* (m. p. 103°) have been already described (Abstr., 1892, 431); the latter dissolves readily in acetic anhydride, and if heated therewith undergoes an isomeric change, being converted into a crystalline mass which melts at 128°.

When ethylic sodium cyanopyruvate is treated with diazobenzene chloride, the compound $CN\cdot CH(N_2Ph)\cdot CO\cdot COOEt$ crystallises out; it forms yellowish-red prisms, melts with decomposition at 149°, and dissolves easily in alcohol, ether, and alkalis, but not in water. Its ammoniacal solution gives an orange-red precipitate with silver nitrate, an orange-yellow precipitate with lead acetate, and a yellowish-white one with mercuric chloride.

Attempts to produce condensation products of the homologues of methylic cyanide with ethylic oxalate proved unsuccessful, and in the paper a theoretical explanation of the failure is offered.

Methylic cyanide does not condense with ethylic succinate under the influence of sodium ethoxide, but benzylic cyanide does, producing the *compound* $C_2H_4(CO\cdot CHPh\cdot CN)_2$, which melts at 156°, and is soluble in alkalis.

The condensation of ethylic oxalate with dimolecular methyl cyanide in the presence of sodium ethoxide produces *ethoxalyldiacetonitrile*, $CN\cdot CH_2\cdot CMe{:}N\cdot CO\cdot COOEt$; this melts at 93°, and dissolves in the usual solvents, including alkalis and hydrochloric acid; when dissolved in absolute alcohol and treated with alcoholic ammonia, the *amide*, $CN\cdot CH_2\cdot CMe{:}N\cdot CO\cdot CONH_2$, is obtained as a white, crystalline powder which melts at 80°, and is insoluble in alcohol and water. A. G. B.

Di-iodides of Tetrolic and Acetylenedicarboxylic acids. By P. Bruck (*Ber.*, **26**, 843—848).—Tetrolic acid, like all unsaturated acids containing a triple bond, and unlike those containing a double bond, unites readily with iodine, best in chloroform solution at 100°. *Di-iodocrotonic acid*, $CMeI{:}CI\cdot COOH$, thus obtained, forms colourless needles melting at 125°, and very sensitive to light; the *silver salt*, $C_3H_3I_2\cdot COOAg$, crystallises in plates with a silky lustre, and is not so sensitive. The *ethylic* salt, $C_3H_3I_2\cdot COOEt$, is a colourless oil which decomposes when boiled; the *amide*, $C_3H_3I_2\cdot CONH_2$, forms lustrous, white needles, and melts with decomposition at 175—176°. When heated with water, the acid yields tri-iodopropylene, $CMeI{:}CI_2$, acetone, and carbonic anhydride; the silver salt, when allowed to remain in contact with water, decomposes into iodallylene, $CMe{:}CI$, carbonic anhydride, and silver iodide.

The di-iodide of acetylenedicarboxylic acid (Abstr., 1892, 431) appears to be *di-iodofumaric acid*, although formed by direct addition, for it gives none of the reactions of a maleïnoïd compound. The *methylic* salt, $C_2I_2(COOMe)_2$, crystallises in brilliant, colourless needles melting at 126°; the *ethylic* salt, $C_2I_2(COOEt)_2$, resembles it, and melts at 88·5°; the *phenylic* salt, $C_2I_2(COOPh)_2$, forms needles melting at 127°; the *chloride*, $C_2I_2(COCl)_2$, long, oblique-angled plates melting at 49°; the *amide*, $C_2I_2(CONH_2)_2$, a colourless, amorphous powder decomposing at 210°; the *anilide*, $C_2I_2(CONHPh)_2$, small needles decomposing at 230°. The silver salt, when boiled with water, breaks up into silver iodide, carbonic anhydride, and formic acid, the oxygen of the air taking part in the reaction. C. F. B.

Action of Nitrous acid on Ethylic Acetonedicarboxylate. By P. Henry and H. v. Pechmann (*Ber.*, **26**, 997—1008).—In addition to the substances previously obtained (Abstr., 1887, 28; 1891, 738), *ethylic dinitrosoacetonecarboxylate peroxide*,

$$COOEt\cdot C\begin{matrix}\diagup\!\!\diagdown CO\!\!\diagup\!\!\diagdown\\ \diagdown\!\!\diagup N\cdot O\cdot O\cdot N\!\!\diagdown\!\!\diagup\end{matrix}C\cdot COOEt,$$

has been got from ethylic acetonedicarboxylate (Abstr., 1891, 671)

by adding the latter to a cooled solution of nitrous anhydride in strong nitric acid. It forms yellow plates melting at 117—118°, and is fairly stable towards acids, but is decomposed by dilute alkalis into nitrous acid and ethylic hydroxyisoxazoledicarboxylate (Abstr., 1891, 738). When reduced, best with sodium hydrogen sulphite, it yields *ethylic hydroxyazoxazinedicarboxylate*,

$$COOEt\cdot C\begin{matrix}-C(OH)\\ N\cdot O\cdot NH\end{matrix}C\cdot COOEt.$$

This forms white, silky needles melting at 169°, gives, like a phenol, a violet colour with ferric chloride, and reacts as a monobasic acid when titrated with an alkali, but yet contains two replaceable hydrogen atoms, as the sequel shows. It yields an *acetyl derivative*, $OH\cdot C_3ON_2Ac(COOEt)_2$, as silky needles melting at 93°. When its silver salt is warmed with an ethereal solution of ethylic iodide, there is obtained an *ethyl derivative*, $OH\cdot C_3ON_2Et(COOEt)_2$, melting at 74°, which reacts as a monobasic acid, and, when treated with benzoic chloride in the presence of soda, yields an *ethylbenzoyl derivative*, $OBz\cdot C_3ON_2Et(COOEt)_2$, as colourless needles melting at 69°; the last compound no longer gives a colour reaction with ferric chloride, unlike the preceding ones, which still contain a C(OH) group. When the silver salt of the ethyl derivative is treated with ethylic iodide, a *diethyl derivative*, $OEt\cdot C_3ON_2Et(COOEt)_2$, is obtained as needles melting at 72°, and giving no colour reaction with ferric chloride; by hydrolysis with soda, it is converted into *diethylhydroxyazoxazinedicarboxylic acid*, which crystallises in nodular aggregates of colourless tables, and melts at 186·5°. When this acid is distilled, best under diminished pressure, it loses carbonic anhydride, and yields a mixture of *ethylethoxyazoxazinecarboxylic acid* and *ethylethoxyazoxazine*, $CH\begin{matrix}-C(OEt)\\ N\cdot O\cdot NEt\end{matrix}CH$; these may be separated by distillation with steam, the latter being readily volatile. The former was obtained in colourless needles; it melts at 109°, and distils to a large extent unchanged; not so its silver salt, which yields the azoxazine. The latter is a colourless oil, boiling at 130·5° and 215° respectively under 32 mm. and 720 mm. pressure. With strong nitric acid, it yields a *nitro-derivative* as colourless plates melting at 69°; the same substance is obtained by the action of nitric acid on the monocarboxylic acid. C. F. B.

Action of Acetic Anhydride on Acetonedicarboxylic acid. By H. v. Pechmann and F. Neger (*Annalen*, **273**, 186—214).—*Carboxydehydracetic acid*, $\begin{matrix}CHAc\cdot CO\\ CO\cdot O\cdot CMe\end{matrix}C\cdot COOH$, is formed when acetonedicarboxylic acid is dissolved in acetic anhydride in the cold, and the solution then warmed for 5—10 minutes; it crystallises in lustrous plates, melts at 154°, and its alcoholic solution gives a brown coloration with ferric chloride. When heated alone, or boiled with alkalis, it is converted into dehydracetic acid (compare Abstr., 1892, 296), but when heated with water it yields dimethylpyrone; it is moderately stable towards oxidising agents, and decolorises alkaline

potassium permanganate only on long keeping. That its constitution is expressed by the above formula, is shown by a comparison of its method of formation with that of the analogous compound described below, as well as by the whole chemical behaviour of the substance; it must be assumed, therefore, that the action of acetic anhydride or of acetic chloride on acetonedicarboxylic acid results first in the formation of a compound of the composition

$$COOH{\cdot}CHAc{\cdot}CO{\cdot}CHAc{\cdot}COOH,$$

by the substitution of two hydrogen atoms in the methylene groups for two acetyl radicles; this compound may then be supposed to undergo intramolecular change into the tautomeric form,

$$COOH{\cdot}CHAc{\cdot}CO{\cdot}C(COOH){:}CMe{\cdot}OH,$$

from which carboxydehydracetic acid is produced by the elimination of 1 mol. H_2O. The properties of carboxydehydracetic acid accord well with this view of its constitution; it is a powerful acid, and has an electrical conductivity about 6000 times as great as that of dehydracetic acid, namely, $\kappa = 3{\cdot}28$ (approximately). Although, on titration, it behaves as a monocarboxylic acid, molecular weight determinations by the cryoscopic method having given results in accordance with those required for the molecular formula $C_9H_8O_6$, it forms two classes of salts, containing one and two equivalents of metal respectively; the latter, however, behave like basic salts.

The *potassium* salt, $C_9H_7O_6K$, is deposited in slender, colourless needles when the acid is dissolved in excess of warm potash, and the solution strongly acidified with acetic acid; it has a neutral reaction, and seems to contain $2H_2O$, which are expelled at 105°. The basic salt, $C_9H_6O_6K_2$, prepared by dissolving the acid in excess of alcoholic potash, and then precipitating with alcohol, crystallises in colourless needles, and has an alkaline reaction. The two *sodium* salts are similar in properties to the potassium compounds. In moderately dilute solutions, both of the normal and basic salts, solutions of many metallic salts produce crystalline or amorphous precipitates. The *methylic* salt, $C_{10}H_{10}O_6$, can be prepared by treating the silver salt with methylic iodide, but it cannot be obtained from the potassium salt under these conditions, nor by treating the acid with methyl alcohol and hydrogen chloride; it crystallises in colourless plates, melts at 65°, and is slowly decomposed by cold water.

The formation of dehydracetic acid from the carboxy-derivative just described leads to the conclusion that dehydracetic acid has the constitution assigned to it by Feist. It follows also that the carboxy-derivative will give the same decomposition products as dehydracetic acid; when heated with concentrated sulphuric acid for example, it yields the lactone of triacetic acid described by Collie, and on treatment with concentrated hydrochloric acid, it is converted into the substance melting at 85° which is obtained from dehydracetic acid under like conditions.

Carboxydehydropropionylacetic acid, $\begin{matrix} CH(COEt){\cdot}CO \\ | \\ CO-O-CEt \end{matrix}\!\!>\!C{\cdot}COOH$, can be obtained by treating acetonedicarboxylic acid with propionic

anhydride; it crystallises in colourless plates, melts at 114—115°, and resembles its homologue, carboxydehydracetic acid, very closely.

Dehydropropionylacetic acid, $\begin{matrix}CH(COEt)\cdot CO\\ |\\ CO\cdot O\cdot CEt{:}CH\end{matrix}$, is formed when a solution of the potassium salt of the preceding compound is evaporated; it crystallises in colourless needles, melts at 72°, and is similar to dehydracetic acid in properties.

Pentabromacetylacetone, $C_5H_3Br_5$, is produced, together with bromodehydracetic acid, when dehydracetic acid or its carboxy-derivative is treated with excess of dry bromine. It crystallises in slender, colourless needles, melts at 79°, and decomposes when heated, when kept, and when boiled with water; it is insoluble in alkalis, and gives no coloration with ferric chloride. Molecular weight determinations in benzene solution by the cryoscopic method gave values in accordance with those required by the above molecular formula; the constitution of the compound is probably expressed by the formula $CH_2Br\cdot CO\cdot CBr_2\cdot CO\cdot CHBr_2$.

The *anilide*, $\begin{matrix}CHAc\cdot CO\\ |\\ CO\cdot O\cdot CMe\end{matrix}\!\!>\!C\cdot CO\cdot NHPh$, crystallises in long, colourless needles, melts at 185°, is soluble in warm sodium carbonate, and its alcoholic solution gives a dark-red coloration with ferric chloride. It is decomposed into aniline and carboxydehydracetic acid by boiling soda.

Phenylmethylacetylpyridonone, $CMe\!<\!\begin{matrix}CH-CO\\ NPh\cdot CO\end{matrix}\!>\!CHAc$, is produced, with evolution of carbonic anhydride, when the preceding compound is distilled under reduced pressure; it crystallises in lustrous plates, melts at 217—218°, and its alcoholic solution gives a red coloration with ferric chloride; it is soluble in soda, and even after the solution has been boiled for a long time, it is precipitated unchanged on adding acetic acid. The formation of this compound from the anilide may be explained by assuming that addition of the elements of water takes place, giving the intermediate product, $COOH\cdot CHAc\cdot CO\cdot C(CO\cdot NHPh){:}CMe\cdot OH$, which, after undergoing tautomeric change, is converted into phenylmethylacetylpyridonone and water.

The *anil*, $C_{21}H_{18}N_2O_4$, can be obtained by boiling carboxydehydracetic acid with excess of aniline; it crystallises in slender, yellow needles, melts at 156—157°, and dissolves unchanged in cold soda, but is decomposed into aniline and carboxydehydracetic acid on boiling the solution.

The *hydrazide*, $\begin{matrix}CHAc\cdot CO\\ |\\ CO\cdot O\cdot CMe\end{matrix}\!\!>\!C\cdot CO\cdot N_2H_2Ph$, prepared by warming carboxydehydracetic acid with phenylhydrazine in glacial acetic acid solution, is a lemon-yellow, crystalline powder, melts at 190—191°, and is soluble in soda, being reprecipitated by carbonic anhydride; it is decomposed by boiling alkalis, and in its solution in concentrated sulphuric acid, ferric chloride and potassium dichromate produce a blue coloration. When carboxydehydracetic acid is boiled for a few minutes with excess of phenylhydrazine, it is converted into a sub-

stance which crystallises in lustrous, colourless needles, and melts at 259—260°; this compound gives no reaction with ferric chloride, is soluble in alkalis, and dissolves in warm, concentrated sulphuric acid with a dark-red coloration.

The experiments described above afford additional evidence that acetonedicarboxylic acid has not the properties of a hydroxy-compound, and no facts pointing to an opposite conclusion have yet been recorded, except those recently brought forward by Perkin (Trans., 1892, 800). The evidence afforded by Perkin's measurements of the magnetic rotation of ethylic acetonedicarboxylate, however, is totally at variance with that obtained by a study of its chemical properties. If, as Perkin concludes, ethylic acetonedicarboxylate, may, under certain conditions, contain a hydroxy-group, the presence of the latter must be capable of proof by suitable chemical methods; hitherto, in spite of numerous attempts, it has been impossible to obtain any indication of its existence, so that ethylic acetonedicarboxylate may be regarded as a ketone for the same reasons as those which apply to the case of ethylic acetoacetate. F. S. K.

Coumalinic acid. By H. v. Pechmann (*Annalen*, **273**, 164—185).—*Methylic methoxymethyleneglutaconate*,

$$COOMe{\cdot}CH{:}CH{\cdot}C(COOMe){:}CH{\cdot}OMe,$$

is formed when coumalinic acid (compare Abstr., 1891, 1457) or its methylic salt is treated with hydrogen chloride under certain conditions which must be strictly observed in order to obtain good results. It crystallises in lustrous plates, melts at 62°, and is insoluble in water, but readily soluble in concentrated mineral acids; it gradually changes into a sticky, pasty mass when kept for a few days, a property common to other hydroxymethylene derivatives. Its alcoholic solution gives no reaction with ferric chloride or copper acetate, but yields a sparingly soluble amido-derivative on treatment with ammonia; when shaken with cold soda, the ethereal salt is converted into the sodium derivative of methylic hydroxymethyleneglutaconate. It is readily reconverted into coumalinic acid by boiling, concentrated hydrobromic acid, and, when treated with bromine, it yields methylic bromocoumalinate.

The formation of methylic methoxymethyleneglutaconate under the conditions mentioned above was hardly to be expected, and, judging from the behaviour of analogous compounds, the production of methylic hydroxymethyleneglutaconate appeared to be more probable; it must therefore be concluded that the methylation of the hydroxy-radicle is determined by the acid character of the hydroxymethylene group, which would appear to behave like the carboxyl-group. This assumption gains in probability by the fact that Claisen's hydroxymethylenecamphor is readily converted into ethoxymethylenecamphor on treatment with alcohol and hydrogen chloride; the ethoxy-compound obtained in this way boils at 265—268°, and is identical with the compound prepared by Claisen by treating hydroxymethylenecamphor with potash and ethylic iodide.

Ethylic ethoxymethyleneglutaconate is not easily obtained in crystals.

Methylic hydroxymethyleneglutaconate,

$$COOMe{\cdot}CH{:}CH{\cdot}C(COOMe){:}CH{\cdot}OH,$$

can be obtained by gently warming the methoxy-compound with dilute soda and decomposing the crystalline sodium derivative with dilute sulphuric acid. It crystallises in lustrous needles, melts at 88—89°, and is readily decomposed by warm water, being converted into methylic trimesate; unlike the methoxy-compound, it does not change even when kept for a long time. Its solution in dilute alcohol gives a bluish-violet coloration with ferric chloride, but not after it has been boiled; it dissolves in alkalis and alkali carbonates, giving colourless solutions which rapidly become yellow and acquire a greenish fluorescence, methylic trimesate being deposited in slender needles. It does not give the ordinary reactions of aldehydes. When boiled with concentrated hydrobromic acid, it yields coumalinic acid, and when heated alone, it is converted into methylic coumalinate and small quantities of other products. The benzoyl derivative,

$$COOMe{\cdot}CH{:}CH{\cdot}C(COOMe){:}CH{\cdot}OBz,$$

prepared by shaking the hydroxy-compound with soda and benzoic chloride, crystallises in colourless needles, melts at 90°, is insoluble in soda, and gives no reaction with ferric chloride.

Methylic amidomethyleneglutaconate,

$$COOMe{\cdot}CH{:}CH{\cdot}C(COOMe){:}CH{\cdot}NH_2,$$

is formed when the methoxy-compound is treated with concentrated alcoholic ammonia; it crystallises in flat, lustrous needles, sinters at 135°, melts at 140—141°, and is soluble in concentrated acids; when treated with acetic anhydride, it yields methylic trimesate.

Methylic methamidomethyleneglutaconate, $C_9H_{13}NO_4$, prepared by treating the methoxy-compound with a concentrated solution of methylamine, crystallises in colourless needles, sinters at 140°, and melts at 143—144°.

Methylic anilidomethyleneglutaconate, $C_{14}H_{15}NO_4$, can be obtained by treating the hydroxy-, methoxy-, or benzoyl-derivative described above with aniline in methyl alcoholic solution, and also by heating the amido-compound with aniline hydrochloride. It is dimorphous; on quickly cooling its solution in hot alcohol, it is deposited in almost colourless needles, which sinter and turn yellow at 107—108°, melting completely at 117—118°; when the needles are left in the mother liquor, they change into small, yellow prisms which melt at 119—120°; the colourless is more readily soluble than the yellow modification, but both are insoluble in alkalis and dilute acids. It is not acted on by acetic anhydride, but, when boiled with soda, it yields small quantities of phenylpyridonecarboxylic acid. The corresponding *paratoluido*-derivative crystallises from alcohol in yellow prisms, and melts at 130°.

Anilidomethyleneglutaconic acid,

$$COOH{\cdot}CH{:}CH{\cdot}C(COOH){:}CH{\cdot}NHPh,$$

is obtained as a canary-yellow precipitate when coumalinic acid is treated with aniline in alcoholic solution at ordinary temperatures; it melts at 120—121°, and is either insoluble in or decomposed by the

ordinary solvents. It is decomposed by hot dilute acids and by boiling alkalis; when treated with dehydrating agents, it yields a well-characterised substance of the composition $C_{12}H_9NO_3$, which is dimorphous, and crystallises in lustrous, yellow plates or in rhombohedra, melting at 220—223°. The methylic hydrogen salt,

$$COOH\cdot CH{:}CH\cdot C(COOMe){:}CH\cdot NHPh,$$

prepared from methylic coumalinate, melts at 140°, and has been previously described as an anil (Abstr., 1884, 1124; 1891, 1457); on prolonged boiling with alcohol, it is converted into a substance which crystallises in lustrous plates melting at 239°, and, when treated with dehydrating agents, it yields a compound of the composition $C_{13}H_{13}NO_4$; the latter crystallises in pale yellow prisms, and melts at 154—155°.

Methylic hydrogen paratoluidomethyleneglutaconate crystallises in sparingly soluble, yellow needles, and melts at 174—178°.

F. S. K.

Formation of Coumalin Rings. By F. Feist (*Ber.*, **26**, 747—764; compare Abstr., 1892, 584).—*Bromodimethylcoumalinic acid*, $C_8H_7BrO_4$, is prepared by heating dimethylcoumalinic acid (isodehydracetic acid) with bromine water; it crystallises from a mixture of benzene and alcohol in lustrous plates which melt at 161—162°, and may be sublimed without decomposition. On hydrolysis with potash, a crystalline, bibasic acid, $\begin{matrix} CMe\text{—}O\text{—}C\cdot COOH \\ \| \qquad\quad \| \\ C(COOH)\cdot CMe \end{matrix}$, is formed, which decomposes at about 260°; at lower temperatures, it is converted into dimethylfurfurancarboxylic acid (see below).

By the action of bromine water on dimethylcoumalinic acid at ordinary temperatures, carbonic anhydride is evolved, and an acid is obtained which melts at 122°, and closely resembles benzoic acid in appearance and properties; its vapour gives a green colour with a pine shaving moistened with hydrochloric acid. The production of this acid is preceded by the hydrolysis of bromodimethylcoumalinic acid and the formation of the hypothetical compound

$$OH\cdot CMe{:}C(COOH)\cdot CMe{:}CBr\cdot COOH,$$

which then decomposes spontaneously into *αβ-dimethylfurfuran-β-carboxylic acid*, $\begin{matrix} O\text{—}CMe \\ | \\ CH{:}CMe \end{matrix}\!\!>\!C\cdot COOH$. This view of its constitution is confirmed by its failure to react with either aqueous or alcoholic ammonia; the electrolytic conductivity, $\kappa = 0{\cdot}00112$, $\mu\infty = 356$, is much lower than that of furfuran-α-carboxylic acid ($\kappa = 0{\cdot}0707$), but similar differences are observed between corresponding compounds of the indole and pyrroline series.

By the action of nitric acid on the preceding carboxylic acid, a non-nitrogenous compound is formed which crystallises in needles, and melts at 178°.

The author failed to observe the production of "bromomesitenlactone" from dimethylcoumalinic acid and bromine water, as described by Hantzsch.

By the action of aqueous ammonia on ethylic dimethylbromocoumalinate, *ethylic bromodimethyl-α-pyridonecarboxylate*,

$$CO<\begin{matrix}NH\cdot CMe\\CBr{:}CMe\end{matrix}>C\cdot COOEt,$$

and *ethylic hydroxydimethyl-α-pyridonecarboxylate*,

$$CO<\begin{matrix}NH\text{---}CMe\\C(OH){:}CMe\end{matrix}>C\cdot COOEt,$$

are produced, together with a third compound which is precipitated from the mother liquors on acidification, melts at 195°, and has not been further investigated. The first salt is sparingly soluble in water, and crystallises in long, white needles melting at 155°; the second crystallises in slender, lustrous plates, becomes red on exposure to air, melts at 118°, and readily sublimes.

By the action of ethylic dimethylbromocoumalinate on alcoholic ammonia, an unstable *ammonium salt*,

$$NH_2\cdot CMe{:}C(COOEt)\cdot CMe{:}CBr\cdot COONH_4,$$

is formed; it is insoluble in ether, and, on treatment with hydrochloric acid, appears to be converted into ethylic bromodimethylpyridonecarboxylate (see above).

Symmetrical methyltrimethenyldicarboxylic acid, $CHMe<\begin{matrix}C\cdot COOH\\\|\\C\cdot COOH'\end{matrix}$ is prepared by the hydrolysis of ethylic dimethylbromocoumalinate with potash; it crystallises from water, and, on sublimation, is deposited in needles which melt at 200° and decompose at slightly higher temperatures. A molecular weight determination by means of the boiling point method in ether agrees with the above formula. The acid is almost 10 times stronger than benzoic acid, as shown from its electrolytic conductivity, $\kappa = 0{\cdot}05815$, $\mu\infty = 356$. It decolorises bromine water and potassium permanganate solution, but does not react with hydrochloric acid or concentrated sulphuric acid; attempts to reduce it or to prepare an anhydride were unsuccessful. The *calcium salt* is deposited in monoclinic crystals containing $3H_2O$; the *barium salt* is crystalline; the *silver*, *lead*, and *mercurous salts* are amorphous. On heating the acid above its melting point, an amorphous, monobasic acid, $C_5H_8O_2$, is formed, of which the *copper* and *lead salts* are sparingly soluble.

Dibromomethyltrimethylenedicarboxylic acid, $CHMe<\begin{matrix}CBr\cdot COOH\\|\\CBr\cdot COOH'\end{matrix}$ is prepared from the trimethenyldicarboxylic acid by the action of bromine in excess at 100°, and is deposited from water in granular crystals melting at 240° with decomposition. *Asymmetrical methyltrimethenyldicarboxylic acid*, $CMe<\begin{matrix}C\cdot COOH\\|\\CH\cdot COOH'\end{matrix}$, is obtained by the reduction of the preceding compound by means of sodium amalgam; it crystallises from water, melts at 189°, and rapidly decolorises potassium permanganate solution and bromine water. The *calcium salt* is very readily soluble in water, and crystallises with $3H_2O$; the crystals are quite different in appearance from those of the calcium salt of the symmetrical acid.

By the action of bromine water on methyltrimethenyldicarboxylic acid at ordinary temperatures, *oxalbromobutyric acid*,

$$COOH{\cdot}CHBr{\cdot}CHMe{\cdot}CO{\cdot}COOH,$$

is formed, and melts at 138—139° with evolution of gas. The *lactonic acid*, $CMe\begin{matrix}<\\<\end{matrix}\begin{matrix}C(COOH)\\CHBr{\cdot}CO\end{matrix}\begin{matrix}>\\>\end{matrix}O$, is prepared by treating symmetrical methyltrimethenyldicarboxylic acid with bromine water at higher temperatures, or by heating the preceding compound above its melting point; it is crystalline, melts at 168°, and is reconverted into the acid on boiling with alkali. On reduction of the bromolactone with sodium amalgam, *oxalbutyrolactonic acid*, $CMe\begin{matrix}<\\<\end{matrix}\begin{matrix}C(COOH)\\CH_2-CO\end{matrix}\begin{matrix}>\\>\end{matrix}O$, is formed, and melts at 141° without decomposition; by the action of hydroxylamine, symmetrical methyltrimethenyldicarboxylic acid appears to be regenerated. J. B. T.

Thiocyanacetamide and Isothiohydantoïn. By A. Miolati (*Gazzetta*, **23**, i, 90—95).—*Thiocyanacetamide*, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}SCN$, is prepared by heating chloracetamide with potassium, ammonium, or barium thiocyanate in alcoholic solution; it separates on cooling the solution, and is ultimately obtained in almost colourless prisms melting at 112°. Ammonia is evolved on heating its solution in caustic soda, and on evaporating its solutions in acids, dioxythiazole is obtained; it yields hydrogen cyanide on reduction with zinc dust and acetic acid, and is soluble in chloroform, but practically insoluble in ether or benzene. The substance described by Claessen (Abstr., 1878, 37) as thiocyanacetamide seems to be merely thiohydantoïn.

Isothiohydantoïn, $\begin{matrix}S\text{———}CO\\|\\CH_2{\cdot}C(NH)\end{matrix}\begin{matrix}\\>\\\end{matrix}NH$, is obtained by dissolving thiocyanacetamide in slightly dilute sulphuric acid, and, after 24 hours, extracting the solution with ether; it forms long, white needles, melts at 71°, and is readily soluble in water or alcohol. Its aqueous solutions give precipitates with salts of silver and mercury. The prolonged action of acids converts it into dioxythiazole.

W. J. P.

Hydurilic and Deoxyamalic acids. By C. Matignon (*Compt. rend.*, **116**, 642—645).—Baeyer regarded hydurilic acid as an ureïde resulting from the condensation of barbituric and dialuric acids. Comparison of the heats of formation of the three acids shows that this change would result in the development of +10·3 Cal. when the acids are in the solid state. The author finds that when finely powdered and intimately mixed barbituric and dialuric acids are heated to the point at which carbonisation begins, hydurilic acid is readily formed. No such change seems to take place with solutions of the two acids.

Since the carbamide residues that exist in malonylcarbamide and tartronylcarbamide also persist in hydurilic acid, it would seem that the latter must have the constitution $C_2H_2\left(\begin{matrix}<\\<\end{matrix}\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}\begin{matrix}>\\>\end{matrix}O\right)_2$.

Deoxyamalic acid.—If finely powdered amalic acid (tetramethylalloxantin) is heated in sealed tubes at 210—220°, deoxyamalic acid is obtained in much larger quantity than when the amalic acid is distilled as in Fischer's method. The acid is almost insoluble in both hot and cold water, but crystallises from hot water in small, brilliant, very hard crystals which seem to be square prisms terminated by pyramids.

The difference between the heats of combustion of amalic and deoxyamalic acid is 40·65 × 2 Cal., a difference which seems to be characteristic of a compound and its hydroxyl-derivative. It would follow that tetramethylalloxantin is the dihydroxy-derivative of deoxyamalic acid. Alloxantin, however, is the dihydroxy-derivative of hydurilic acid, and hence it follows that deoxyamalic acid is the tetramethyl derivative of hydurilic acid, and its constitution is $C_2H_2\left(<\begin{matrix}CO\cdot NMe\\CO\cdot NMe\end{matrix}>CO\right)_2$.

The difference between the heats of combustion of hydurilic and deoxyamalic acids is 165·8 × 4 Cal., and it has previously been shown that 165·8 Cal. is the characteristic difference for methyl derivatives when the methyl is united with nitrogen.

This view is supported by the following facts: Deoxyamalic acid decomposes boiling silver nitrate solution and yields an oxidation product which gives a blood-red coloration with ferric chloride. Solutions of the acid or its salts give with ferric chloride a beautiful green coloration, the formation of which is prevented by acids and alkalis. In presence of excess of ferric chloride, the green colour becomes red on boiling. These reactions are strictly analogous to those given by hydurilic acid. Hydurilic acid when oxidised yields alloxan, whilst deoxyamalic acid yields dimethylalloxan. The author has shown that hydurilic acid has three distinct acid functions. The tetramethyl derivative ought only to have two such functions, and as a matter of fact deoxyamalic acid yields a dipotassium salt, which forms hard, transparent, slightly yellowish crystals, but no tripotassium compound is produced. C. H. B.

Thiophen of Crystallisation. By C. Liebermann (*Ber.*, **26**, 853—854).—Triphenylmethane, dibromo-β-dinaphthyl oxide, and α-truxillic acid chloride crystallise with thiophen, forming transparent, colourless crystals, which rapidly lose thiophen in the air and become opaque. The compounds with the first two substances have the composition $CHPh_3 + C_4H_4S$ and $C_{20}H_{12}Br_2O + C_4H_4S$ respectively. C. F. B.

Electrolytic Reduction of Nitrobenzene dissolved in Sulphuric acid. By A. A. Noyes and A. A. Clement (*Ber.*, **26**, 990—992).—A current of 3 ampères (potential 5 volts) was passed for 15 hours at 80—90° through a solution of 1 part of nitrobenzene in 4 parts of concentrated sulphuric acid. Paramidophenolorthosulphonic acid was formed, the yield being 40 per cent. of the theoretical. If only 0·1 part of water is added, no sulphonic acid is

produced, but the sulphate of paramidophenol, as Gattermann and Koppert found.

Neither orthonitrotoluene nor α-nitronaphthalene yields an insoluble sulphonic acid; both yield a sulphate of a readily oxidisable base. C. F. B.

Diiodometaxylene obtained from Iodometaxylene and Sulphuric acid. By A. Töhl and E. Bauch (*Ber.*, **26**, 1105—1108; compare Abstr., 1890, 1106).—The formation of durene by the action of methylic iodide on the diiodo-xylene (*loc. cit.*) shows that the latter has the constitution [$Me_2 : I_2 = 1 : 3 : 4 : 6$]. The iodometaxylenesulphonic acid (Abstr., 1891, 73) forms a *sodium* salt which crystallises in silky needles containing $2H_2O$, a *sulphochloride* melting at 74°, a *sulphonamide* melting at 176°, and *sulphanilide* melting at 153°.

The diiodo-xylene dissolves slowly in fuming sulphuric acid forming *tetraiodo-xylene* melting at 128°, and a *diiodo-xylenesulphonic acid*. The latter gives a *sodium* salt which crystallises with $2H_2O$, a *barium* salt which is sparingly soluble in water, a *sulphochloride* melting at 85—87°, and a *sulphonamide* melting at 242—245° with decomposition. The sodium salt, on reduction with zinc dust and ammonia, gives 1 : 3 : 4-metaxylenesulphonic acid; this shows that a shifting of one of the iodine atoms of the diiodo-xylene must have taken place during the sulphonation. A. R. L.

Reactions of Iodomesitylene. By A. Töhl and R. Eckel (*Ber.*, **26**, 1099—1104).—By shaking iodomesitylene (Abstr., 1892, 96) with concentrated sulphuric acid, *diiodomesitylene*, which crystallises in yellowish-white needles and melts at 82—83°, is obtained, together with *mesitylenesulphonic acid*, the *sulphonamide* of which melts at 142°. Fuming sulphuric acid converts both iodomesitylene and diiodomesitylene into *triiodomesitylene*, which crystallises in stout, yellowish-white prisms, and melts at 208°, and mesitylenesulphonic acid. When sulphuric anhydride is allowed to condense into a flask containing iodomesitylene, the products are diiodomesitylene and iodomesitylenesulphonic acid; whilst from diiodomesitylene and sulphuric acid there are formed triiodomesitylene and the last-mentioned sulphonic acid. The barium salt crystallises with 1 mol. H_2O, and begins to decompose at 130°, the *lead* salt is very sparingly soluble in water, and the *sulphonamide* melts at 156°.

Nitroiodomesitylene is obtained by the action of a mixture of fuming and ordinary nitric acid on iodomesitylene; it crystallises in white needles, and melts at 73—74°. *Dinitroiodomesitylene*, melting at 205—206°, is formed by the action of fuming nitric acid on iodomesitylene. *Nitrodiiodomesitylene*, melting at 183°, is obtained by the action of a mixture of ordinary and fuming nitric acid on diiodomesitylene. When triiodomesitylene is warmed with a mixture of nitric and sulphuric acids, dinitriodomesitylene and trinitromesitylene (m. p. 230°) are formed. Chlorosulphonic acid converts iodomesitylene and diiodomesitylene into trichloromesitylene; the latter is also formed, together with the intermediate *chlorodiiodomesitylene* (m. p.

167°) and *dichloriodomesitylene* (m. p. 183°), when mono- and di-iodomesitylene are treated with chlorine. A. R. L.

Paradiethylbenzene. By H. Fournier (*Bull. Soc. Chim.* [3], **7**, 651—653).—The product of the action of ethylic bromide on benzene in the presence of aluminium chloride contains, contrary to Voswinckel's statement, more metadiethylbenzene than of the para-derivative. The mixture is sulphonated and then converted into barium salt (Voswinckel, Abstr., 1889, 38); on crystallising this from water, the meta-derivative separates out, whilst the impure para-derivative which remains in solution is purified by conversion into the cadmium salt (Abstr., 1889, 493). To regenerate the hydrocarbon, the sodium salt is heated with phosphoric acid of 60° B. Paradiethylbenzene melts at −35°. The *tribromo*-derivative melts at 105—106°, and the *tetrabromo*-derivative melts at 157°. A. R. L.

Behaviour of Halogen Derivatives of ψ-Cumene towards Sulphuric acid. By A. Töhl and A. Müller (*Ber.*, **26**, 1108—1113).—Symmetrical fluoro-ψ-cumene (Abstr., 1888, 362) is only sulphonated by warming it with concentrated sulphuric acid, and, unlike the chloro-, bromo-, and iodo-derivatives, one *sulphonic acid* only is formed; this melts at 115—116°, forms a *barium* salt sparingly soluble in water, which crystallises with $1H_2O$, a *sodium* salt crystallising with $4H_2O$, a *sulphochloride* melting at 36—37°, and a *sulphonamide* melting at 174°.

When fluoro-ψ-cumene is treated with chlorine in the presence of iodine, fluorodichloro-ψ-cumene, which crystallises in long, silky needles, and melts at 150°, represents the solid portion of the product; whilst the liquid portion is converted by chlorosulphonic acid into a *fluorochloro-ψ-cumenesulphonic acid*, which forms a *sodium* salt sparingly soluble in water, an oily *sulphochloride*, and a *sulphonamide* melting at 171°. The fluorochloro-ψ-cumene, regenerated from the sodium salt by heating it with concentrated hydrochloric acid at 180°, is a liquid boiling at 205° and solidifying when cooled; on treatment with fuming sulphuric acid, it yields fluorodichloro-ψ-cumene and fluoro-ψ-cumenesulphonic acid (see above). By the action of bromine on fluoro-ψ-cumene there are formed *fluorodibromo-ψ-cumene* melting at 143—144°, and a liquid which, when treated with chlorosulphonic acid, yields *fluorobromo-ψ-cumenesulphonic acid*; the *sodium* salt crystallises with $2H_2O$, and the *sulphonamide* melts at 149°. The regenerated fluorobromo-ψ-cumene yields with sulphuric acid fluorodibromo-ψ-cumene and fluoro-ψ-cumenesulphonic acid.

A mixture of ordinary and fuming nitric acid converts fluoro-ψ-cumene into *nitrofluoro-ψ-cumene*, a liquid which solidifies at 5°; whilst fuming nitric acid converts it into an acid and *dinitrofluoro-ψ-cumene* which crystallises in colourless needles and melts at 74—76°. *Fluoro-ψ-cumidine* is prepared by reducing nitrofluoro-ψ-cumene with iron and acetic acid; its *acetyl* derivative melts at 118°. By the diazo-reaction, it may be converted into *fluoriodo-ψ-cumene*, an oil which did not solidify when cooled to 0°, and decomposes with liberation of iodine on treatment with sulphuric acid. A. R. L.

Pentethylbenzene. By H. Fournier (*Bull. Soc. Chim.* [3], **7**, 653—654).—When pentethylbenzene (Jacobsen, Abstr., 1889, 40) is heated in an oil-bath at 120° with benzylic chloride and a little aluminium chloride, the product treated with water, extracted with ether, and the ethereal solution distilled, *benzylpentethylbenzene*, $C_6Et_5{\cdot}CH_2Ph$, may be isolated from the portion passing over above 300°. It crystallises in white needles, melts at 88—89°, and boils above 360°. A. R. L.

Compounds of Alkali Phenoxides with Phenol. By de Forcrand (*Compt. rend.*, **116**, 586—588).—Calorimetric determinations indicate that potassium phenoxide combines with phenol to form the compound $C_6H_5{\cdot}OK,3C_6H_5{\cdot}OH$, but forms no definite compound containing a higher or a lower proportion of phenol.

Sodium phenoxide forms two compounds, $C_6H_5{\cdot}ONa,3C_6H_5{\cdot}OH$ and $C_6H_5{\cdot}ONa,6C_6H_5{\cdot}OH$.

It is noteworthy that, in additive compounds such as alcoholates, phenolates, or hydrates, the ratio 1 : 3 is very common; that frequently a potassium derivative forms only one such additive compound, whilst the corresponding sodium derivative forms two or more; and that, although the sodium derivative may combine with a larger number of molecules of the phenol, alcohol, &c., the additive compound formed by the potassium derivative is usually more stable.

C. H. B.

Symmetrical Dimethoxyquinone. By G. Ciamician and P. Silber (*Ber.*, **26**, 784—786).—Symmetrical trimethoxybenzene is readily prepared by fusing either methylhydrocotoïn or methylpyrocotoïn with potash (compare this vol., i, 417); on oxidation with chromic anhydride in glacial acetic acid solution, it is converted into symmetrical dimethoxyquinone (m. p. 249°), which is identical with Hesse's "quinone." J. B. T.

Metamidodialkylorthotoluidines. By A. Bernthsen (*Ber.*, **26**, 992—993).—A reply to Weinberg, this vol., i, 265.

Compounds containing Double Linking between Nitrogen and Carbon. By A. Hantzsch (*Ber.*, **26**, 926—929).—No case of stereoisomerism has been observed in the examination of the following compounds.

The *compound* $OMe{\cdot}C_6H_4{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}NMe_2$ is obtained by mixing anisyl phenylketochloride (1 mol.) with amidodimethylaniline (3 mols.) in chloroform solution. It crystallises in sulphur-yellow crystals, melts at 116°, is resolved into the ketone and base by mineral acids, and yields a hydrochloride which is decomposed by water.

Phenylbenzimidophenyl ether, $OPh{\cdot}CPh{:}N{\cdot}Ph$, is obtained by mixing benzanilidoimide chloride and sodium phenoxide suspended in absolute ether. It forms colourless crystals, melts at 104°, and is decomposed by warm, concentrated hydrochloric acid into aniline and phenylic benzoate.

Tolylbenzimidophenyl ether, $OPh{\cdot}CPh{:}N{\cdot}C_6H_4Me$, melts at 120°, and yields a crystalline hydrochloride, which is decomposed by water.

The *compound* OPh·CPh:N·COOEt is obtained by converting ethylic benzoylcarbamate into the chloride, CPhCl:N·COOEt, with phosphoric chloride, and then treating it with sodium phenoxide. It melts at 91°.

Benzoylurethane cannot be prepared from sodium urethane and benzoic chloride. When these compounds are mixed, they yield *ethylic dibenzoylcarbamate*, NBz_2·COOEt, which crystallises in large, rhombic tablets, and melts at 103°, and a compound of the composition $C_{17}H_{13}NO_3$, which is more soluble in alcohol than ethylic dibenzoylcarbamate, crystallises in white needles, and melts at 190°.

E. C. R.

Azo-derivatives of Catechol. By O. N. Witt and F. Mayer (*Ber.*, **26**, 1072—1076).—The author has shown (D.R.-P. 49,872 and 49,979) that β-naphthaquinol combines with diazo-compounds to form azo-dyes, a fact which stands in antithesis to Griess' rule that such compounds can only be obtained from metadihydroxy-, and metadiamido-derivatives.

Benzeneazocatechol, $C_6H_3(OH)_2$·N_2Ph, is obtained by mixing an alcoholic solution of catechol with a concentrated solution of diazobenzene chloride, and after a while pouring the mixture on to ice; the precipitate is crystallised first from a solution of sodium acetate, and subsequently from alcohol. When its solutions are allowed to slowly cool, it separates in garnet-red needles having a blue surface-lustre, whilst by rapidly cooling its solutions, it separates in golden leaflets which, if left in contact with the liquid, pass into the red modification. It melts at 165° with decomposition, is soluble in alkalis, and dyes cotton mordanted with alumina golden-yellow.

Paratolueneazocatechol, C_6H_4Me·N_2·$C_6H_3(OH)_2$, forms copper-red, lustrous leaflets, melts at 175° with decomposition, and is more readily soluble in water than the benzene derivative.

Paranitrobenzeneazocatechol, NO_2·C_6H_4·N_2·$C_6H_3(OH)_2$, colours alumina mordants red and iron and chromium mordants deep brown; it is reduced to dihydroxyamidoazobenzene by ammonium sulphide. The *diacetyl* derivative melts at 126—127°.

The *compound* SO_3Na·C_6H_4·N_2·$C_6H_3(OH)_2$ is obtained by dropping freshly-prepared diazobenzeneparasulphonic acid into an aqueous solution of catechol, and precipitating with sodium acetate; its aqueous solution gives crystalline precipitates on the addition of calcium and barium salts, and intense colorations with salts of the iron group. Wool mordanted with alumina is dyed golden-yellow, and mordanted with chromium, reddish-brown.

Benzoylcatechol, OH·C_6H_4·OBz, forms lustrous, white needles, melts at 130—131°, and forms an azo-compound which when warmed with alkali yields benzeneazocatechol.

A. R. L.

Action of Hydrazine Hydrate on Organic Halogen Compounds. By R. v. Rothenburg (*Ber.*, **26**, 865—868).—It has been previously shown by Schöfer (*Inaug. Diss., Kiel*, 1892) that hydrazine hydrate does not act on ethylic chloracetoacetate in a similar manner to ammonia, but yields hydrazine monohydrochloride and nitrogen as the sole recognisable products. The author finds that with benzoic

chloride it behaves like ammonia, yielding the benzoylhydrazine already described, together with either the mono- or di-hydrochloride of hydrazine. With methylic iodide, it yields ethylene and hydrazine dihydriodide, with ethylic iodide, ethylene and trihydrazine dihydriodide, and with isoamylic iodide, the same salt and isoamylene. Benzylic chloride yields, in addition to hydrazine monohydrochloride, a mixture of dibenzyl, stilbene, and tolane, the latter being probably derived from the benzal chloride usually present in commercial benzylic chloride.

Chloroform is not acted on by hydrazine hydrate, even at the boiling point, whilst iodoform appears to undergo a slight reduction.

H. G. C.

New Method of preparing Unsymmetrical Derivatives of Phenylhydrazine. By O. Widman (*Ber.*, **26**, 945—948).—When β-acetylphenylhydrazine, NHPh·NHAc, is acetylated with acetic chloride, a second acetyl group enters in the α-position, and when the diacetyl derivative is boiled with dilute acid, hydrolysis occurs and the β-acetyl group is displaced. In this way, several α-acidyl derivatives of phenylhydrazine, including some compounds already known, have been prepared; the melting points of these are given, and further experimental details are promised. A. R. L.

The Hydrochlorides of Stereoisomeric Aldoximes. By A. Hantzsch (*Ber.*, **26**, 929—932).—The hydrochlorides of both synaldoximes and antialdoximes are converted by water into antialdoximes, and by aqueous alkali carbonates or ammonia into synaldoximes. This seems to indicate that the two stereoisomerides yield identical hydrochlorides. From the following results, however, it is proved that this is not the case. When anisantialdoxime and cuminantialdoxime are converted into hydrochlorides by treating their ethereal solutions with hydrogen chloride, and when the dry salts are treated with a solution of ammonia in absolute ether, anisantialdoxime (m. p. 61°) and cuminantialdoxime (m. p. 58°) are regenerated. Similarly the synaldoximes after the same treatment are recovered as synaldoximes.

If anisantialdoxime hydrochloride, suspended in dry ether, is treated with dry ammonia, it yields pure anis-synaldoxime. Under the same conditions, cuminsynaldoxime yields cuminantialdoxime, and paranitrobenzantialdoxime and paranitrobenzsynaldoxime yield a mixture of the two isomerides. E. C. R.

Oxidation and Sulphonation of Organic Compounds by Ammonium Hydrogen Sulphate. By M. Lachaud and C. Lepierre (*Bull. Soc. Chim.* [3], **7**, 649—651).—When naphthalene, pyridine, aniline, &c., are added to fused ammonium hydrogen sulphate, they are dissolved, and the product is soluble in water. In the case of aniline, on heating the melt to between 200° and 350°, a series of colouring matters, ranging from red, violet, and blue to black, are formed, some of which dye silk directly. A. R. L.

Unsymmetrical Dibenzylthiocarbamide. By G. Mazzara (*Gazzetta*, **23**, i, 37—43).—On mixing benzene solutions of thio-

carbonyl chloride and dibenzylamine, heat is evolved, and a mixture of dibenzylamine hydrochloride and *dibenzylthiocarbamic chloride*, $CSCl{\cdot}NBz_2$, separates; the latter forms a yellow, hygroscopic, crystalline mass, which melts at 49—50°, and is very soluble in benzene, alcohol, or chloroform. When heated at 100° with alcoholic ammonia, it yields unsymmetrical dibenzylthiocarbamide. This compound forms colourless laminæ, melts at 134—135°, and when prepared by heating dibenzylamine thiocyanate is also obtained colourless, and of the melting point given above, not, as stated by Salkowski (Abstr., 1891, 1474) in yellow crystals melting at 141°.

Dibenzylamine thiocyanate is obtained by the action of aqueous thiocyanic acid on dibenzylamine, or by mixing solutions of dibenzylamine hydrochloride and potassium thiocyanate; it melts at 156—157°, not at 164—165°, as stated by Salkowski (*loc. cit.*), and is far more soluble in water than unsymmetrical dibenzylthiocarbamide. On heating either the thiocyanate or the thiocarbamide at 140° for some time, a mixture of the two isomerides is obtained; the conversion of the one substance into the other is therefore a reversible change at this temperature. The thiocyanate gives the well-known red coloration with ferric chloride, whilst the thiocarbamide does not.

W. J. P.

Gallanilide and its Triacetyl and Tribenzoyl Derivatives. By P. Cazeneuve (*Compt. rend.*, **116**, 698—700).—Aniline gallate, when heated at 105—110°, loses carbonic anhydride before losing water, thus forming gallanilide. If, however, gallotannic acid is heated with excess of aniline at about 150° for an hour, gallanilide is formed, and after treating the product with dilute hydrochloric acid, can be crystallised from dilute alcohol. After repeated crystallisation, it forms large lamellæ, which lose 2 mols. H_2O at 100°, and when anhydrous have the composition $C_6H_2(OH)_3{\cdot}CO{\cdot}NHPh$. It melts at 205° without any marked discoloration, and without any evolution of gas. It is only slightly soluble in cold water, but dissolves readily in hot water, and the solution gives a blue coloration with ferric chloride. It dissolves easily in alcohol of 93°, and also somewhat readily in ether of 65°, but it is insoluble in chloroform, benzene, and light petroleum. It dissolves better in alkalis, forming coloured solutions, but the alteration is only partial. It is not affected when boiled with sodium hydroxide solution for 10 minutes, and it is only slowly attacked by dilute sulphuric and hydrochloric acids. When heated at 150° for an hour with twice its weight of concentrated hydrochloric acid, gallanilide yields gallic acid and aniline. With acetic anhydride, it yields a triacetyl derivative, which crystallises from alcohol in very light, small, white needles melting at 160—161° to a colourless liquid, which decomposes with evolution of acetic acid. The acetyl derivative gives no coloration with ferric chloride. Benzoic chloride yields a tribenzoyl derivative, which crystallises from boiling toluene in small, white needles melting at 181°. This compound is insoluble in most solvents, and cannot be distilled without decomposition.

C. H. B.

Quercetin Derivatives. By J. Herzig and T. v. Smoluchowski (*Monatsh.*, **14**, 39—52 and 53—55; compare Abstr., 1888, 1309; 1890, 64; 1891, 1386.—*Constitution of Fisetol.*—The method of preparing fisetol from fisetin has been already described (*loc. cit.*). Fisetol, $C_8H_8O_4$, contains three hydroxyl groups, and the fourth oxygen atom is evidently present as a carbonyl or formyl group, since the compound reacts with phenylhydrazine. As it is evidently a resorcinol derivative, it must have the constitution: (i) $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot OH$; (ii) $C_6H_3(OH)_2\cdot CH(OH)\cdot COH$; or, less probably,

(iii) $COH\cdot C_6H_2(OH)_2\cdot CH_2\cdot OH$.

Methylfisetol, $C_8H_6O_2(OMe)_2$, when heated in a reflux apparatus with alcoholic phenylhydrazine for three hours, gives the compound $C_{18}H_{18}O_3N_2$, which crystallises from hot alcohol in shining yellow scales, and melts at 55—57°.

With hydroxylamine hydrochloride, ethylfisetol forms the equally well characterised compound $C_{12}H_{17}NO_4$, which crystallises from dilute alcohol in beautiful, white needles, and melts at 105—107°. On oxidation with potassium permanganate in alkaline solution, ethylfisetol yields a mixture of *ethylresorcylglyoxylic acid* and *ethylresorcylic acid*. The former, $C_{10}H_{17}O_5$, crystallises from water and benzene in white scales, melts at 65—68°, contains only one of the ethoxyl groups present in ethylfisetol, and is converted on ethylation into the diethoxy-acid, $C_8H_4O_3(OEt)_2$, which crystallises from benzene in stout, white needles, and melts at 128—130°. It readily reacts with hydroxylamine, giving rise to a compound which melts at about 150°. The acid, $C_8H_6O_5$, from which it is derived must therefore have the formula $COH\cdot C_6H_2(OH)_2\cdot COOH$, if the first or second of the constitutions suggested above for fisetol be correct. The probability of the third constitution for fisetol being correct is extremely small, since that would assume the oxidation of an alkyl group to carboxyl, whilst a formyl-group remained intact, a most improbable occurrence. Each of the oxidation products of ethylfisetol contains only one ethoxyl-group; the second ethoxyl-group present in ethylfisetol is, therefore, most probably contained in the side chain, which is removed by oxidation. It follows that ethylfisetol must contain free hydroxyl, and that it should be represented by one of the following formulæ:—

$OEt\cdot C_6H_3(OH)\cdot CO\cdot CH_2\cdot OEt$ or $OEt\cdot C_6H_3(OH)\cdot CH(OEt)\cdot CHO$.

The latter, however, is most improbable, since no carboxylic acid corresponding to it is found amongst the products of oxidation.

Composition of Quercitrin.—The authors have made a number of analyses of quercitrin, and have obtained results which closely agree with the formula $C_{21}H_{22}O_{12}$, previously found by Liebermann and Hamburger (Abstr., 1879, 944). Quercitrin is resolved by hydrolysis into equal molecular proportions of quercetin and rhamnose.

G. T. M.

Isomeric Amidobenzoic acids. By O. de Coninck (*Compt. rend.*, **116**, 510—512 and 588—591).—The author has determined the quantity of each of the three isomeric amidobenzoic acids dissolved

in two hours, at a temperature of about 10°, by 10 c.c. of various solvents, namely, hydrochloric, hydrobromic, and hydriodic acids, dilute nitric, sulphuric, and acetic acids, glacial acetic acid, dilute ammonia solution, dilute lime water, dilute baryta solution, light petroleum, benzene, carbon bisulphide, ethylic acetate, and water. The experiments with water were made at 12—14°. Light petroleum boiling at 35—65° dissolves no trace of any of the three isomerides.

The results show that the three isomerides differ distinctly in solubility, but differ in pairs, one of the three being either more or less soluble in a particular solvent than the other two. For example.

	Ortho-.	Meta-.	Para-.
Hydrochloric acid	0·929	1·283	0·980
Hydrobromic acid	0·1753	0·0504	0·0751
Hydriodic acid	0·589	0·574	1·193
Nitric acid, dilute.....	0·8775	0·1950	0·1484
Sulphuric acid, dilute....	0·380	0·336	0·382
Acetic acid, „	0·0370	0·0764	0·0454
Water.....	0·0340	0·0568	0·0336

In the case of the alkali solvents, this differing in pairs is less distinctly marked. C. H. B.

Orthomethamidobenzoic acid. By G. FORTMANN (*J. pr. Chem.* [2], **47**, 400).—Orthomethamidobenzoic acid melts at 179°, but begins to soften at 170°, which has heretofore been given as its melting point. By treating its hydrochloride with sodium nitrite in water, *nitrosorthomethamidobenzoic acid*, $COOH{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$, is obtained; it crystallises in small prisms, and melts at 128°.

Orthacetylmethamidobenzoic acid is a crystalline powder which melts at 192°. A. G. B.

Optically Active Cinnamic acid Dibromides. By C. LIEBERMANN and A. HARTMANN (*Ber.*, **26**, 829—833; compare this vol., i, 268).—Inactive cinnamic acid dibromide, $C_9H_8Br_2O_2$, has, as before described, been separated into dextro- and lævo-rotatory constituents by crystallising the strychnine salts of these acids,

$$C_{21}H_{22}N_2O_2,C_9H_8Br_2O_2,$$

from an alcoholic solution containing the base and acid in the proportions $C_{21}H_{22}N_2O_2 : 2C_9H_8Br_2O_2$, the crystallisation being started by the introduction of a few crystals of the particular constituent which it was desired to separate.

By repeated application of this process, the inactive dibromide was split up into two constituents, with rotations $[\alpha]_D = +67—67{\cdot}5°$ and $-65{\cdot}7°$ respectively. The + and − dibromides appear to form complementary hemihedral crystals, which have the same crystallographical constants as the inactive substance; the latter, however, exhibits some additional faces. No evidence has yet been obtained of the existence of a third and a fourth active dibromide, such as are predicted by Van't Hoff's theory. C. F. B.

Optically Active Cinnamic acid Dichlorides. By C. Liebermann and H. Finkenbeiner (*Ber.*, **26**, 833—834).—Inactive cinnamic acid dichloride has been separated, although not so readily, into its optically active constituents by the method adopted in the case of the corresponding dibromide (see preceding abstract). The process of fractionation is not yet complete; the maximum rotations so far obtained are $[\alpha]_D = +67{\cdot}3°$ and $-44°$. C. F. B.

Orthonitrobenzyl Derivatives. By C. Beck (*J. pr. Chem.* [2], **47**, 397—400).—Orthonitrobenzylphthalimide melts at 207° (Gabriel gives 217·5—219°; Abstr., 1887, 1037).

Orthonitrobenzylsuccinimide, $C_{11}H_{10}N_2O_4$, is made by heating an alcoholic solution of succinimide and sodium hydroxide with orthonitrobenzyl chloride for 12 hours in a reflux apparatus; it crystallises in nacreous laminæ, and melts at 130°.

The best method for preparing orthonitrobenzylamine sulphate is to heat the phthalimide with sulphuric acid, filter off the phthalic acid, make alkaline with caustic soda, extract with ether, and shake the ethereal solution with dilute sulphuric acid; it crystallises in long, white tables. The normal salt is sparingly soluble in alcohol, whilst the acid salt dissolves freely in alcohol and water. The alcohol is easily obtained from the amine by the action of nitrous acid.

A. G. B.

Conversion of Phthalide Derivatives into those of $\alpha\gamma$-Diketohydrindone. By S. Gabriel and A. Neumann (*Ber.*, **26**, 951—955).—A method of preparing phthalylacetic acid,

$$\begin{matrix} C_6H_4 \\ | \\ CO{\cdot}O \end{matrix}\!\!>\!C{:}CH{\cdot}COOH,$$

is described in which potassium acetate is used instead of sodium acetate, whereby the yield is augmented. When the acid is made into a paste with wood spirit, and poured into a solution of sodium in wood spirit, the *disodium salt* of $\alpha\gamma$-diketohydrindenecarboxylic acid, $C_6H_4\!<\!\begin{matrix} CO \\ CO \end{matrix}\!>\!CNa{\cdot}COONa + H_2O$, separates as a yellow precipitate; the *sodium* salt, $C_{10}H_5O_4Na + 2H_2O$, is precipitated on the addition of acetic acid to an aqueous solution of the disodium salt. When the disodium salt is warmed with dilute hydrochloric acid, carbonic anhydride is evolved and $\alpha\gamma$-diketohydrindene (Abstr., 1888, 1194) is obtained; whilst by heating it in a sealed tube at 100° with methyl alcohol and methylic iodide, dimethyl-$\alpha\gamma$-diketohydrindene (Abstr., 1889, 1068) is formed. Benzalphthalide and ethylidenephthalide behave in a similar manner to phthalylacetic acid.

A. R. L.

Diphenylsulphonethylic and Ditolylsulphonethylic Oxides. By R. Otto and J. Tröger (*Ber.*, **26**, 944—945).—The hydroxyethylphenylsulphone prepared by Otto (*J. pr. Chem.* [2], **30**, 171 and 321) is now found to contain *diphenylsulphonethylic oxide*,

$$(SO_2Ph{\cdot}CH_2{\cdot}CH_2)_2O;$$

it melts at 69—70°. The *homologous compound* (m. p. 83—84°) was also separated from hydroxyethyltolylsulphone (*loc. cit.*). The authors regard the ethers as formed at the same time as the alcohols, and discard the view that they have been derived from the latter by spontaneous dehydration. A. R. L.

Anilides of Benzene- and Paratoluene-sulphonic acids; Phenyl- and Paratolyl-sulphonoxysulphobenzide. By R. Otto (*J. pr. Chem.* [2], **47**, 367—374).—Phenylsulphoneanilide, paratolylsulphoneanilide, and phenylsulphonemethylanilide (m. p. 79—80°) have been re-examined, and their crystallographical measurements, together with those of the undermentioned anilides, are recorded.

Paratolylsulphonemethylanilide, $NMePh{\cdot}SO_2{\cdot}C_7H_7$, melts at 94—95°; it is insoluble in water, but dissolves easily in boiling alcohol, benzene, and ethylic acetate.

Phenylsulphonethylanilide, $NEtPh{\cdot}SO_2Ph$, is a yellowish, viscid oil, insoluble in water, but soluble in ether, alcohol, and benzene.

Paratolylsulphonethylanilide, $NEtPh{\cdot}SO_2{\cdot}C_7H_7$, melts at 87—88°, is insoluble in water, but soluble in boiling alcohol, boiling benzene, and ethylic acetate.

The above anilides were prepared from the corresponding substituted anilines and sulphonic chlorides.

Phenylsulphonoxysulphobenzide, $SO_2(O{\cdot}C_6H_4{\cdot}SO_2Ph)_2$, is prepared from oxysulphobenzide and benzenesulphonic chloride; it forms aggregates of silky crystals, melts at 131—132°, and dissolves in hot alcohol and ethylic acetate, but not in water.

Paratolylsulphonoxysulphobenzide, from oxysulphobenzide and paratoluenesulphonic chloride, forms feebly lustrous, ill-defined needles, melts at 171—172°, and dissolves in boiling ethylic acetate and boiling glacial acetic acid. A. G. B.

Non-existence of Stenhouse's Phenylthiosulphuric acid. Sulphonic acids of Phenyl Sulphide. Bunte's Salt. By R. Otto and J. Tröger (*Ber.*, **26**, 993—996).—The substance obtained by heating phenyl sulphide with an equal volume of strong sulphuric acid on the water bath is not phenylthiosulphuric acid, $OH{\cdot}SO_2{\cdot}SPh$, as Stenhouse stated, but *thiodibenzenedisulphonic acid*, $C_{12}H_8S(SO_3H)_2$; its *barium salt*, with H_2O, and *chloride*, melting at 157°, were prepared. By acting on phenyl sulphide (1 mol.) with chlorosulphonic acid (2 mols.), an isomeric (or identical?) disulphonic acid was obtained, of which the *chloride* melts at 157°, but the *barium salt* crystallises with $3H_2O$. With 1 mol. of chlorosulphonic acid, a *thiophenylbenzenesulphonic acid*, $SPh{\cdot}C_6H_4{\cdot}SO_3H$, was obtained; the *chloride* melts at 66—68°, the *amide* at 129—130°.

Bunte's salt (sodium ethylic thiosulphate) can be obtained in a yield of 90 per cent. by shaking ethylic bromide with a saturated solution of sodium thiosulphate at 35° until the former has all disappeared, evaporating the solution, and extracting the residue with alcohol. C. F. B.

"Leucotin" and Cotogenin. By G. Ciamician and P. Silber (*Ber.*, **26**, 777—784; compare Abstr., 1892, 62 and 873).—Jobst and Hesse obtained a compound, which they termed "leucotin," from paracoto bark; the authors have reinvestigated this substance, and find that it consists of a mixture of almost equal parts of methylprotocoïn, $CH_2<^{O}_{O}>C_6H_3\cdot CO\cdot C_6H_2(OMe)_3$, and methylhydrocotoïn, $C_6H_2Bz(OMe)_3$, together with about 10 per cent. of paracotoïn. The last of these is removed by treatment of "leucotin" with potash, and the other two compounds are separated by repeated extraction of the residue with ether at the ordinary temperature; methylprotocotoïn being the more readily soluble.

Cotogenin, $C_{14}H_{14}O_5$ (m. p. 210°), was prepared by Jobst and Hesse by fusing "leucotin" or "oxyleucotin" (methylprotocotoïn) with potash, orthodihydroxybenzaldehyde [1 : 3 : 4] being also formed; the cotogenin obtained by the fusion of pure methylprotocotoïn with potash melts at 217°, but is otherwise identical in properties with Jobst and Hesse's compound, and proves to be *dihydroxybenzoyltrimethoxybenzene*, $C_6H_3(\overset{3,4}{OH})_2\cdot\overset{1}{C}O\cdot C_6H_2(\overset{1,2,3}{OMe})_3$. The *diacetate* crystallises in stellate prisms melting at 120°. The presence of orthodihydroxybenzaldehyde in the products of fusion could not be detected. J. B. T.

Carbazacridines. IV. Oxidation of Phenylcarbazacridine. By D. Bizzari (*Gazzetta*, **23**, i, 1—9; compare Abstr., 1891, 219; 1892, 617).—Phenylcarbazacridine is slowly oxidised by permanganate in hot acetic acid solution; the addition of much water to the solution causes the separation of a substance, which is probably a diphenyleneimidoketone, $CO<^{C_6H_3}_{C_6H_3}>NH$. It forms minute, yellow crystals melting at 177—179°, and is soluble in alcohol, ether, and benzene. Boiling caustic alkalis do not decompose it, and it is precipitated unchanged by water from its solution in sulphuric acid; it gives the normal molecular weight by the cryoscopic method in benzene. Potassium nitrite acts readily on its acetic acid solution, forming a *nitroso*-derivative, which is precipitated by water; it forms minute, yellow crystals melting at 128·5°, is soluble in alcohol, acetic acid, ether, or benzene, and probably contains the group :N·NO. The *acetyl* derivative is obtained in long, white needles or laminæ melting at 152°. Diphenyleneimidoketone, when fused with potash, yields an *acid*, and when treated with hydroxylamine, gives a small yield of another substance; these products have not yet been investigated. The author quotes further arguments in support of the formula previously assigned by him to phenylcarbazacridine. W. J. P.

Isocarbostyril. By A. Fernau (*Monatsh.*, **14**, 59—70).—Anhydrous isoquinoline is heated with potassium, in the form of fine wire, for 4—5 hours at 100°, and afterwards for 1 hour at 170—180°. The product is poured into a dish, and allowed to remain exposed to the air for 12—15 hours, whereby the violet-brown mass becomes a

reddish oil. The oil is dissolved in alcohol, the alcohol evaporated, and the residue mixed with water and then exhausted with ether. The ethereal solution, on evaporation, gives an oil, from which crystals of Bamberger's isocarbostyril, $C_6H_4<\begin{matrix}CH{:}CH\\ |\\ CO\cdot NH\end{matrix}$, separate (yield 22—25 per cent.). This compound crystallises slowly from alcohol in large, monoclinic needles; $a : b : c = 1{\cdot}8500 : 1 : 1{\cdot}25995$. It melts at 209°, gives a *platinochloride*, $(C_9H_7NO)_2,H_2PtCl_6$, crystallising in yellow needles, and, on distillation with zinc-dust, is again converted into isoquinoline. On heating with potassium hydroxide and methylic iodide, isocarbostyril is converted into the *pseudomethylic salt*, C_9H_6ONMe, which melts at 54°, and does not give methylic iodide when heated with hydriodic acid. The *true methylic salt*, C_9H_6NOMe, which is obtained by treating the silver salt with methylic iodide, is an oil boiling at about 240°, and readily loses methyl when heated with hydriodic acid.

The oil, mentioned above, from which the isocarbostyril separated, gave, on fractional distillation, a portion boiling at 233—235°; but analysis did not enable the author to determine whether this consisted of *dihydroisoquinoline* or of a mixture of isoquinoline with *tetrahydroisoquinoline*. The behaviour of isoquinoline towards the alkali metals and oxygen is noteworthy, as, under like conditions, quinoline is converted into diquinolyl. G. T. M.

Constitution of the Truxillic acids. By C. Liebermann and H. Sachse (*Ber.*, **26**, 834—838; compare Abstr., 1890, 1424).—*β*-Truxillic acid, since it yields benzile when oxidised, must be a geometrical variety of the first of the two possible structural formulæ given below, which represent the acid as a tetramethylene derivative.

(1) $\begin{matrix}CHPh\cdot CH\cdot COOH\\ |\quad\quad |\\ CHPh\cdot CH\cdot COOH\end{matrix}$, (2) $\begin{matrix}\quad\quad CHPh\cdot CH\cdot COOH\\ \quad\quad |\quad\quad |\\ COOH\cdot CH—CHPh\end{matrix}$;

and further, it must be one of those varieties in which the two COOH groups are situated on the same side of the tetramethylene ring (like phthalic acid in the benzene series), for it yields an internal anhydride, as the molecular weight of the latter, determined cryoscopically, proves; and this anhydride yields, with resorcinol, a *fluorescein*, $CO<\begin{matrix}O—\\ C_{16}H_{14}\end{matrix}>C[C_6H_3(OH)_2]_2$, as an amorphous, brownish-red powder; with aniline, an *anil*, $C_{16}H_{14}<\begin{matrix}CO\\ CO\end{matrix}>NPh$, forming colourless needles melting at 180°, and converted by cold alcoholic potash into the *anilic acid*, $COOH\cdot C_6H_{14}\cdot CO\cdot NHPh$; this forms white crystals melting at 197° and yields a *barium salt*, $(C_{24}H_{20}NO_3)_2Ba$; with phenylhydrazine in acetic acid solution, it gives a *phenylhydrazide*, $C_{16}H_{14}<\begin{matrix}CO\\ CO\end{matrix}>N_2HPh$, forming colourless crystals melting at 218°.

γ-Truxillic acid must have the COOH groups on opposite sides of the ring, for, although it yields an internal anhydride, this anhydride gives no fluorescein with resorcinol, and with aniline yields no anil,

but an *anilic acid*, forming white needles melting at 220°, together with some *anilide*, $C_6H_{14}(CO{\cdot}NHPh)_2$, crystallising in needles and melting at 255°.

α-Truxillic anhydride yields no fluoresceïn, and must be an external anhydride, for its molecular weight, cryoscopically determined, corresponds with the formula $(C_{36}H_{30}O_7)_3$. C. F. B.

Formation of Cycloïd Compounds from 1 : 5-Diketones: Synthesis of a Structural Isomeride of Camphor. By E. KNOEVENAGEL (*Ber.*, **26**, 1085—1090).—The author has employed two methods for the synthesis of 1 : 5-diketones. The first consists in the action of ethylic salts of unsaturated acids on compounds of the type of ethylic acetoacetate, and the second in heating ethylic acetoacetate with an aldehyde in the presence of a primary amine (Hantzsch). The formation of pyridine derivatives from 1 : 5-diketones and hydroxylamine, an example of which has recently been given in the case of benzamarone (this vol., i, 352), is by no means a general reaction.

Those 1 : 5-diketones which contain a methyl group in the sixth position from one of the carbonyl groups are, when treated with condensing agents, converted into derivatives of Δ_2-ketotetrahydrobenzene (compare Hagemann, this vol., i, 393). Thus, from *ethylic deoxybenzoïnbenzalacetoacetate* and alkali there results 3 : 4 : 5-*triphenyl-*Δ_2*-ketotetrahydrobenzene*, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CPh{\cdot}CHPh\\CO\text{—}CH_2\end{matrix}>CHPh$, which exists in two modifications, melting at 138° and 180° respectively; and when ethylic benzylidenediacetoacetate is suspended in alcohol, and treated with hydrogen chloride, the *compound*

$$CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{\cdot}CH(COOEt)\\CO\text{—}CH(COOEt)\end{matrix}>CHPh,$$

which melts at 86°, is formed. The compound obtained from *ethylic isobutylidenediacetoacetate* is denominated by the author *metacamphor*, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{\cdot}CH_2\\CO\text{—}CH_2\end{matrix}>CH{\cdot}CHMe_2$; it is a liquid resembling camphor and menthol in its odour, and boils at 244—245° (uncorr.). The corresponding derivative of the para-series may be identical with ordinary camphor. A. R. L.

Derivatives of Phenolphthaleïn and of Fluoresceïn. By A. HALLER and A. GUYOT (*Compt. rend.*, **116**, 479—482).—When carefully dried phenolphthaleïn (1 mol.) is heated at 130° with phenylic isocyanate (2 mols.), *phenolphthaleïn bisphenylcarbamate*,

$$\begin{matrix}C_6H_4\\CO{\cdot}O\end{matrix}>C(C_6H_4{\cdot}O{\cdot}CO{\cdot}NHPh)_2,$$

is obtained. It crystallises from boiling benzene in white needles which melt at 135°. It is not attacked by boilin water but when treated with alkalis, or when heated above its melting point, it yields phenolphthaleïn and symmetrical diphenylcarbamide.

Fluoresceïn bisphenylcarbamate is obtained in a similar way, and forms pale yellow, microcrystalline grains very slightly soluble in most ordinary solvents, but somewhat soluble in acetone. It melts at 195°, and splits up into fluoresceïn and phenylcarbamide.

Dibenzylphenolphthaleïn is obtained by the action of benzylic chloride on an alcoholic solution of sodiophenolphthaleïn, and crystallises from a mixture of benzene and alcohol in beautiful, blue, nacreous leaflets melting at 150°. It is only slightly soluble in boiling alcohol or in ether, but dissolves readily in benzene. When heated with alcoholic potash, it seems to be hydrolysed, but after a time the solution deposits the original compound. No oxime is formed when it is heated at 100° with hydroxylamine hydrochloride and potassium hydroxide. When an alcoholic solution of the dibenzylphenolphthaleïn is heated with zinc and hydrochloric acid, it yields a thick, transparent liquid which solidifies to a brittle, and sometimes crystalline, mass. This product is insoluble in alkalis, and when treated with acetic acid and potassium dichromate, it again yields dibenzylphenolphthaleïn.

The general properties of dibenzylphenolphthaleïn, and more particularly the fact that it yields no oxime, seem to support Baeyer's view as to the constitution of the phthaleïns. C. H. B.

Octonaphthylene and Octonaphthenic Alcohol. By S. Jukoffsky (*J. Russ. Chem. Soc.*, **24**, 201—205).—The chloride, $C_8H_{15}Cl$, boiling at 167—168°, obtained amongst the chlorination products of octonaphthene, was heated in a sealed tube with 1 part of dry sodium acetate and 2 parts of glacial acetic acid for 48 hours at 200°. After pouring into water and neutralising, the upper layer was separated, dried, and fractionated. The fraction 115—140° was distilled repeatedly over sodium, after which it boiled for the most part between 117° and 121°, this portion being the octonaphthylene already obtained by Yakoffkin. An attempt was made to prepare the hydrocarbon C_8H_{12} by the addition of 2 atoms of bromine to the octonaphthylene, and subsequent separation of 2HBr by heating with acetic acid and sodium acetate. No hydrocarbon, however, was obtained in this way, the product of the action boiling at a high temperature, and consisting chiefly of the ethereal salt, $CH_3{\cdot}COOC_8H_{15}$; sp. gr. 0·9275 at 0°/0°, b. p. 195—200°. From this acetate, the corresponding alcohol, $C_8H_{15}{\cdot}OH$, was obtained by hydrolysis, and dried by means of caustic baryta. It boils at 182·5—184·5°, and has the sp. gr. 0·8920 at 0°/0°. J. W.

Condensation of Metaphenylenediamine with β-Naphthol. By F. Gaess and E. Elsaesser (*Ber.*, **26**, 976—981).—By melting the two substances together at 250°, a mixture of mono- and di-β-naphthylmetaphenylenediamine is obtained. The substance described by Ruhemann (Abstr., 1882, 391) as the dinaphthyl compound is really the mononaphthyl derivative.

Mono-β-naphthylmetaphenylenediamine, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_7$, forms long, colourless needles with an asbestos-like lustre, melts at 128°, boils at about 320° under 40 mm. pressure, and exhibits in solution a

greenish-blue fluorescence; the *hydrochloride*, $C_{16}H_{14}N_2,HCl$, forms white needles which redden when kept; the *dihydrochloride* is a white powder, which is decomposed by boiling water with formation of the monochloride; both chlorides, when heated, turn red, and melt at 210°; an alcoholic solution of the dihydrochloride fluoresces reddish-blue. The *sulphate*, $(C_{16}H_{14}N_2,)_2,H_2SO_4$, crystallises in lustrous, rhombic plates, with reddish-blue fluorescence. The *picrate*, $C_{16}H_{14}N_2,C_6H_3N_3O_7$, forms golden plates melting with decomposition at 180°. The *monacetyl derivative*, $NHAc\cdot C_6H_4\cdot NHC_{10}H_{17}$, is obtained in nodular groups of colourless needles melting at 135°, and fluorescing reddish-blue in alcoholic solution; the *diacetyl derivative*, $NHAc\cdot C_6H_4\cdot NAc\cdot C_{10}H_7$, crystallises in bundles of colourless, non-fluorescent needles melting at 147—148°. The *benzoyl derivative*, $NHBz\cdot C_6H_4\cdot NH\cdot C_{10}H_7$, forms large, thin, nacreous plates melting at 173°; the *dibenzoyl derivative*, $NHBz\cdot C_6H_4\cdot NBzC_{10}H_7$, was obtained as colourless, rhombic tables melting at 213°; neither of these compounds fluoresces in solution.

Di-β-naphthylmetaphenylenediamine, $C_6H_4(NH\cdot C_{10}H_7)_2$, forms colourless needles, fluoresces reddish-blue in solution, melts at 192°, and boils with partial decomposition above 460° under 45 mm. pressure. The *dihydrochloride*, $C_6H_4(NH\cdot C_{10}H_7,HCl)_2$, is a white, crystalline powder which turns grey and loses hydrochloric acid when kept; it melts at 210°, turning red, and is deprived of all its hydrochloric acid by boiling with water. No picrate could be obtained. The *diacetyl derivative*, $C_6H_4(NAc\cdot C_{10}H_7)_2$, forms colourless plates melting at 175°; the *dibenzoyl derivative*, $C_6H_4(NBz\cdot C_{10}H_7)_2$, crusts of colourless prisms melting at 215°; neither fluoresces in solution. C. F. B.

Preparation of Naphthidine. By F. Reverdin and C. De La Harpe (*Chem. Zeit.*, **16**, 1687).—Naphthidine (Abstr., 1886, 245) is obtained when α-naphthylamine (100 grams) is dissolved in 88 per cent. sulphuric acid (1000 grams), ferric oxide (55 grams) added at 40°, and the mixture heated, first at 75° and subsequently at 100°, for several hours. The product is poured into water, the precipitate collected, washed with warm water, converted into base with alkali, and crystallised from alcohol. The various mother liquors appear to contain an isomeric base. The tetrazo-colours obtained by combining diazotised naphthidine with amines, phenols, &c., are feeble.

A. R. L.

Derivatives of α-Naphthylacetylene and of β-Naphthylacetylene. By J. A. Leroy (*Bull. Soc. Chim.* [3], **7**, 644—649).—α-Naphthylacetylene (Abstr., 1292, 495) combines with one equivalent of sodium or potassium in the presence of ether, forming yellow, pulverulent compounds which, when suspended in anhydrous ether and treated with dry carbonic anhydride, yield the alkali salt of *α-naphthylpropiolic acid*. The free acid crystallises from hot water or carbon bisulphide in white, silky needles which become yellowish on exposure to light, melts at 138—139° with decomposition, and yields α-naphthylacetylene when heated with water in a sealed tube at 125°. The barium salt crystallises with 1 mol. H_2O.

α-Ethylnaphthalene is readily chlorinated by the action of chlorine in sunlight; the portion of the product boiling at 185° (40 mm.) is the dichloro-derivative, and when this is treated with alcoholic potash at 110°, it is converted into α-naphthylacetylene.

The derivatives of β-naphthylacetylene dealt with in this paper have all been previously described (*loc. cit.*). A. R. L.

Substantive Cotton Dyes from Diamidophenanthraquinone. By S. Litthauer (*Ber.*, **26**, 848—851).—It has been thought that meta-substituted derivatives of benzidine yield only dyes which do not dye the cotton fibre directly, but a consideration of the cases of benzidinesulphone, diamidodiphenylene oxide, and diamidocarbazole shows that this rule does not hold if the substituting groups form a ring. A further confirmation of this is obtained from the fact that diamidophenanthraquinone yields substantive dye stuffs.

Phenanthraquinonedisazoresorcinol, $\begin{matrix}CO\cdot C_6H_3\cdot N_2\cdot C_6H_3(OH)_2\\ |\\ CO\cdot C_6H_3\cdot N_2\cdot C_6H_3(OH)_2\end{matrix}$, obtained by adding a diazotised solution of the diamidoquinone to resorcinol, is violet when moist, dark green and of metallic lustre when dry. *Phenanthraquinonedisazo-β-naphthol*, obtained in a similar manner from β-naphthol, is bluish-red when moist, green and metallic when dry. *Phenanthraquinonedisazo-α-naphthol*, from α-naphthol, is rather redder in colour when moist. *Phenanthraquinonedisazo-β-naphthylamine*, from β-naphthylamine, is bluish-red when moist.

C. F. B.

Action of Sulphuric acid on Menthol. By Tolotchko (*J. Russ. Chem. Soc.*, **24**, 249—250).—By acting in the cold with sulphuric acid on menthol, the author was unable to prepare the menthene of Walther and Beckmann, but obtained instead of it a hydrocarbon, $C_{10}H_{20}$, *mentholene*, which exhibits the properties of the polymethylenes. It boils at 168—169° under a pressure of 760 mm., and has the sp. gr. 0·8066 at 0°/0°. Bromine is only slowly decolorised by the hydrocarbon, hydrogen bromide being evolved. A weak solution of potassium permanganate was not entirely decolorised after two weeks, although the hydrocarbon was shaken up with it daily for 8—10 hours at 50°. The action of sulphuric acid on borneol is under investigation by the author. J. W.

Camphor. By G. Oddo (*Gazzetta*, **23**, i, 70—85, 85—90).—The author shows that the same camphocarboxylic acid is obtained from camphor (compare Brühl, Abstr., 1892, 200), and from bromocamphor by treatment with sodium, and subsequently with carbonic anhydride; it is quantitatively converted into bromocamphocarboxylic acid by the action of bromine on its absolute alcoholic solution (compare de Santos and Silva, Abstr., 1874, 70). On boiling the bromo-acid with water, ordinary bromocamphor melting at 76° is obtained.

In an appendix to this paper, the author defends the constitutional formula previously suggested by him for camphor (Abstr., 1892, 724), and criticises adversely those proposed by Brühl (*loc. cit.*), and by Collie (Abstr., 1892, 864).

On adding sodium nitrite solution to camphocarboxylic acid, suspended in water, isonitrosocamphor is formed, and is then partially converted into the camphorquinone described by Claisen and Manasse (Abstr., 1889, 619). Camphocarboxylic acid should, therefore, contain the group $C_8H_{14}<\begin{matrix}CH\cdot COOH\\CO\end{matrix}$. W. J. P.

Ethereal Salts of Camphoric acid. By J. W. Brühl (*Ber.*, **26**, 1097—1099).—A reply to Walker (*Ber.*, **26**, 600).

Derivatives of Campholenic acid. By W. Thiel (*Ber.*, **26**, 922—926).—The nitrile of campholenic acid is a colourless liquid, and boils at 224° (uncorr.), and not at 216—218°, as stated by Goldschmidt and Zürrer (*Ber.*, **17**, 2070). It is converted into potassium campholenate by prolonged boiling with alcoholic potash, but a pure preparation cannot be obtained unless the traces of campholenamide, which is also formed, are extracted from the aqueous alkaline solution with ether. Pure campholenic acid distils at 255—256°.

Campholene is obtained by boiling campholenic acid in a reflux apparatus. It boils at 129—130·5°. The author was unable to obtain a pure product by the distillation of calcium campholenate with soda-lime. When treated with bromine in the presence of water, hydrogen bromide is evolved and resinous products are obtained. In the absence of water, when treated with bromine in chloroform solution at −15°, it yields a *dibromide*, $C_{10}H_{16}Br_2O_2$, which melts at 96·5—97°.

Isohydroxycamphoric acid, $C_{10}H_{16}O_5$, is obtained together with acetic acid by oxidising campholenic acid with chromic acid. It crystallises from chloroform in slender needles, from water in large, vitreous prisms, melts at 129—130·5°, is bibasic, and yields easily soluble salts. It is isomeric with α-hydroxycamphoric acid (*Annalen*, **145**, 212) and camphoric acid (*Annalen*, **163**, 333).

Isocamphoronic acid, $C_9H_{14}O_8$, is obtained by the further oxidation of the preceding acid. It crystallises from nitric acid in large prisms, melts at 166—167°, and is tribasic. E. C. R.

Glucosides of the Convolvulaceæ. By N. Kromer (*Chem. Centr.*, 1893, i, 310—312; from *Pharm. Rund.*, **31**, 625—630, 641—646, 657—662, 673—678, 689—694, 705—712, 721—723, 737—743, 753—758, and 769—771).—Scammonin, $C_{68}H_{106}O_{42}$, the resinous glucoside of the roots of *Convolvulus scammonia*, melts at 123·68° (corr.), has $[\alpha]_D = -23·06°$, and is a white, amorphous powder, soluble in alcohol, ether, chloroform, &c., insoluble in light petroleum and water. It is an acid anhydride, and by the action of alkalis is hydrolysed into the bibasic *scammonic acid*, $C_{22}H_{44}O_{13}$, an amorphous, yellow substance of strongly acid reaction, which decomposes carbonates.

Scammonin is oxidised by nitric acid into oxalic, valeric, and butyric acids, carbonic anhydride, and an acid melting at 101°, which is isomeric with sebacic acid. Potassium permanganate oxidises

scammonin to oxalic and valeric acids, and the monobasic *scammonolic acid*, $C_{16}H_{30}O_2$, which forms a wavellite-like mass melting at 65·8°. When hydrolysed with mineral acids, scammonin yields *scammonole*, $C_{16}H_{30}O_3 + \frac{1}{2}H_2O$ (2 mols.), which melts at 63—77°, valeric acid (4 mols.), and a sugar (6 mols.), which is closely related to mannose; the latter is fermentable, does not crystallise, and has a rotatory power of +17·78° at 19°. 0·00763 gram of the sugar reduces 1 c.c. of Fehling's solution. The *pentabenzoyl* compound, $C_6H_7O_6Bz_5$, is a white powder, and melts at 63°; the phenylhydrazine compound, forms clear, yellow needles, and melts at 191°.

Turpethin, $C_{76}H_{128}O_{36}$, the glucoside of the roots of *Ipomœa turpethum*, is an amorphous, yellow powder, colourless in thin layers, and melts at 146·8° (corr.); it has a rotatory power of −30·14°, and is sparingly soluble in chloroform, soluble in alcohol and acetic acid. When treated with alkalis, it yields *turpethic acid*, a yellow, hygroscopic mass. By oxidation with nitric acid, turpethin yields oxalic, isobutyric, and sebacic acids and carbonic anhydride, whilst potassium permanganate oxidises it to oxalic, isobutyric, and turpetholic acids. When hydrolysed with mineral acids, it yields isobutyric acid (1 mol.), *turpethole*, $C_{16}H_{30}O$(?$C_{16}H_{30}O_3$), a substance forming feathery, interlaced crystals, and melting at 85·76° (1 mol.), glucose (3 mols.), and a viscid, liquid acid, which was not isolated but gave a silver salt, $C_{15}H_{27}O_5Ag$.

Turpetholic acid, $C_{16}H_{32}O_4$, is obtained, as above mentioned, and also by the action of alkalis or their carbonates on turpethole. It forms a hard, white, crystalline mass, melts at 88·4°, and is soluble in alcohol, sparingly soluble in ether; turpethole seems to be the anhydride of turpetholic acid. A. J. G.

Active Principles of Bryony Root. By Masson (*J. Pharm.* [5], **27**, 300—307).—Bryony root is extracted with cold 3 per cent. hydrochloric acid, the extract precipitated by tannin, the purified precipitate extracted with alcohol, and the bryonin liberated in an impure state by zinc oxide. It is purified by dissolving it in hydrochloric acid, removing the acid by dialysis, drying the residue, dissolving in alcohol, and precipitating the pure substance with ether.

Bryonin, $C_{34}H_{48}O_9$, is a white, very bitter, amorphous powder, and dextrorotatory, $[\alpha]_D = +41·25°$. It is precipitated by tannin and ammoniacal lead acetate, and is hydrolysed by dilute sulphuric acid into glucose and a resinous substance, *bryogenin*, $C_{14}H_{19}O_2$, which melts at 210°, and is dextrorotatory, $[\alpha]_D = +105°$. This dissolves in concentrated sulphuric acid to a red solution, which changes to purple on heating, and from which a purple precipitate is then obtained on the addition of water. The residue left after extracting the root with water yields a resin on further extraction with alcohol. *Bryoresin*, $C_{37}H_{66}O_{18}$, is a red, amorphous substance which softens at 15°, but becomes liquid only at 250°. It forms compounds with alkalis, lead, and copper. Jn. W.

Saponins. By R. Kobert (*Chem. Centr.*, 1893, i, 32, 33; from *Pharm. Post*, **25**, 1141—1144, 1168—1171; compare Abstr., 1891,

1532). A large number of glucosides are comprehended under the name of saponin substances, and are characterised by the properties that their aqueous solutions froth strongly, that they prevent the deposition of finely-divided precipitates, &c. Chemically, they belong to several series, but those of the general formulæ $C_nH_{2n-8}O_{10}$ are especially numerous, and of these the following list is given:—$C_{17}H_{26}O_{10}$: Saponin, senegin, Quillaja-sapotoxin, Sapindus-sapotoxin, Gypsophila-sapotoxin, Agrostemma-sapotoxin. $C_{18}H_{28}O_{10}$: Saponin II, digitonin (Schmiedeberg), saporubin, senegin, assamin. $C_{19}H_{30}O_{10}$: Saponin III, quillajic acid, polygalic acid, Herniaria-saponin. $C_{20}H_{32}O_{10}$: Cyclamin, digitonin (Paschkis), Merck's quillajic acid, Sarsaparilla-saponin. $C_{22}H_{36}O_{10}$: Sarsasaponin. $C_{26}H_{44}O_{10}$: Parillin. $C_{26}H_{50}O_{10}$: Melanthin. There is some doubt as to whether certain of these substances really belong to this series, but it is probable that dulcamarin, $C_{22}H_{31}O_{10}$, and syringin, $C_{17}H_{26}O_{10}$, will on further investigation be found to do so. Some other glucosides of quite different composition, for instance, paridin, $C_{16}H_{28}O_7$, judged by their properties, belong to the saponin substances.

The original paper contains a classified list of the plants, 140 in number, in which saponin substances have been detected.

A. J. G.

Action of Phosphoric Chloride on Santonin. By J. Klein (*Ber.*, **26**, 982—983).—The product of the action of phosphoric chloride on santonin has not the formula $C_{15}H_{16}OCl_2$ (this vol., i, 112), but $C_{15}H_{15}Cl_3O_2$; the third chlorine atom seems to be in the ring. The substance melts with decomposition at 171—172°, and yields a hydrazone with phenylhydrazine; it has the properties of an unsaturated compound. The facts favour the conclusion that santonin is a δ-lactone, and contains two carbon atoms which are capable of forming a double bond between them, which double bond is probably in the lactone ring.

C. F. B.

Derivatives of Santonin. By J. Klein (*Ber.*, **26**, 1069—1071).—A reply to Cannizzaro (this vol., i, 364).

Fumaroïd and Maleïnoïd Structure of some Derivatives of Santonins. By G. Grassi-Cristaldi (*Gazzetta*, **23**, i, 65—69).—The author considers that santononic and isosantononic acids or santonone and isosantonone, are respectively fumaroïd and maleïnoïd isomerides; he is still engaged on experimental work in connection with this subject.

W. J. P.

Action of Hydrochloric acid on the Santonones. Bisdihydrosantinic acid. By G. Grassi-Cristaldi (*Gazzetta*, **23**, i, 58—65; compare Abstr., 1892, 869; this vol., i, 110).—*Methylic bisdihydrosantinate*, $C_{32}H_{38}O_4$, is prepared by passing hydrogen chloride through a solution of santonone or isosantonone in methyl alcohol; after purification, the salt is obtained in colourless, thin needles melting at 131°; it is soluble in alcohol, ether, benzene, ethylic acetate, and chloroform, sparingly so in light petroleum. It has a specific rota-

tion $[\alpha]_D = +97{\cdot}1°$ in a 2·65 per cent. benzene solution at 24°, and has a normal molecular weight in freezing benzene or acetic acid.

Bisdihydrosantinic acid, $C_2\left(\begin{array}{l}\text{CMe}=\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\\ \text{CH}\cdot\text{CMe}:\text{C}\cdot\text{CH}:\text{C}\cdot\text{CHMe}\cdot\text{COOH}\end{array}\right)_2$, is obtained by boiling its methylic salt with alcoholic baryta, adding hydrochloric acid, and crystallising the precipitated acid from alcohol; it forms colourless, silky needles melting at 215°, and has a specific rotatory power $[\alpha]_D = +34{\cdot}9°$ in a 1·65 per cent. acetic acid solution at 24°. The acid is sparingly soluble in alcohol, glacial acetic acid, benzene, or ether; it is insoluble in carbonates or caustic alkalis in the cold, and its salts are decomposed by passing a current of carbonic anhydride through their solutions. Nearly all the salts are insoluble in water, with the exception of those of the alkali metals.

W. J. P.

Methylbrazilin. By J. Herzig (*Monatsh.*, **14**, 56—58).—Methylbrazilin, which melts at 137—138°, proves to be a trimethyl compound having the formula $C_{16}H_{10}O_5Me_3$, and not a tetramethyl compound, as stated by Schall and Dralle (compare Abstr., 1888, 295; 1889, 55, 1004).

G. T. M.

Constitution of Five-membered Rings. By E. Bamberger (*Annalen*, **273**, 373—379).—A reply to Ciamician and Hinsberg.

F. S. K.

Synthesis of Oxypyridine and Oxypiperidine Bases. By A. Ladenburg (*Ber.*, **26**, 1060—1069; compare Abstr., 1890, 67; 1891, 1092).—The author has prepared 1-methylpipecolylalkine from pure picoline, and confirms the physical constants previously given by him for it and its derivatives, so that Lipp's compound (Abstr., 1891, 1245) was, perhaps, a stereoisomeride.

1-*Methylvinylpiperidine*, $C_5NH_9Me\cdot C_2H_3$, is obtained by gradually adding concentrated sulphuric acid in the cold to a solution of hydrotropine in glacial acetic acid and heating the mixture at 190°. It is a colourless liquid having the odour of coniine and tropidine, boils at 159—162°, and is soluble in an equal volume of water; the platinochloride melts at 197—198°.

The author has failed to obtain tropine by the oxidation of hydrotropine with various reagents. When an aqueous solution of hydrotropine is boiled with chloranil, a *base* is produced giving an aurochloride and mercurochloride differing only in melting point from those of tropine; whilst by oxidising benzoylhydrotropeïne with hydrogen peroxide and boiling the product with potash, a similar *base* is obtained yielding a *mercurochloride* melting at 210°, an *aurochloride* melting at 180°, and a crystalline *methochloride*. This base, which may be a mixture of tropine and hydrotropine, is provisionally named *α-tropine*; it yields a compound (*α-homatropine*) with mandelic acid, having mydriatic properties. The author contends that, although he has failed to synthesise tropine, the last-described base so closely resembles that compound in its properties, that the experiments may be taken as a confirmation of his previously published views on the constitution of tropine.

The remainder of the paper is polemical, and the author upholds his formulæ against those proposed by Merlin (Abstr., 1892, 359), which he regards as based on fictitious evidence. He is able to agree with Merlin in regard to the constitution of one compound only, namely, that of tropilidene. A. R. L.

Resolution of β-Pipecoline into its Optical Isomerides. By A. Ladenburg (*Ber.*, **26**, 1069).—Experiments, which are still in progress, have proved that β-pipecoline may be resolved into its optical isomerides by crystallising its tartrate (compare this vol., i, 442). A. R. L.

Penthiazolines. By G. Pinkus (*Ber.*, **26**, 1077—1084).—Penthiazolines are obtained more readily from thiamides and trimethylene chlorobromide than when trimethylene bromide is used, probably on account of the lower melting point of the former.

Mesophenylpenthiazoline, $CPh\begin{matrix}S\cdot CH_2\\ N\cdot CH_2\end{matrix}>CH_2$, is obtained by heating together thiobenzamide and trimethylene chlorobromide. It crystallises from water in small, white needles, melts at 44—45°, is volatile with steam, but cannot be distilled alone without decomposition. The *platinochloride* melts at 185°, and the *mercurochloride* at 140—142°. When heated in a sealed tube with hydrochloric acid at 200—210°, it yields benzoic acid and amidopropyl mercaptan, together with hydrogen sulphide; whilst homotaurine and its benzoyl derivative are formed when it is heated on the water-bath with bromine water. The *methiodide*, $C_{10}H_{11}NS,MeI$, is obtained by treating the new base with methylic iodide; it melts at 184°, is decomposed by hydrochloric acid and bromine water in a manner analogous to the parent compound, yields an oily *compound*, $C_{22}H_{28}N_2S_2O_3$, on treatment with alkali, and when shaken with moist silver chloride, the *methochloride* is formed, the *platinochloride* of which melts at 191°.

Mesorthotolylpenthiazoline is an oil, and *mesoparatolylpenthiazoline* melts at 52—53°.

Mesobenzylpenthiazoline, prepared from phenylacetic thiamide and trimethylene chlorobromide, is a liquid of sp. gr. 1·113 at 15°, having an odour resembling that of hemlock.

Mesomethylpenthiazoline is obtained from thiacetamide and trimethylene chlorobromide; the yield is poor. It is a colourless liquid miscible with water, boils at 173° (757 mm.); the *picrate* melts at 138°. Mesomethylthiazoline (Abstr., 1891, 816) can be prepared from thiacetamide and ethylene dibromide.

A *compound*, $C_8H_{16}ClBrN_2S_2O_2$, melting at 102—103° is obtained by heating xanthogenamide, $OEt\cdot CS\cdot NH_2$, with trimethylene chlorobromide. A. R. L.

Formation of Isoquinoline. By E. Fischer (*Ber.*, **26**, 764—765; compare P. Fritsch, this vol., i, 366).—Benzoylacetalamine hydrochloride is dissolved in fuming sulphuric acid, and the dark-red solution allowed to remain for 24 hours; on dilution and neutralisation, isoquinoline is obtained; it was identified by means of the

platinochloride. With concentrated sulphuric acid, the aldehyde yields a base which is volatile with steam, and is probably a hydroisoquinoline.

Benzoylacetalamine, on treatment with fuming sulphuric acid, also yields a crystalline condensation product which is being further investigated. J. B. T.

Triphenylpiperazine. By L. Garzino (*Gazzetta*, **23**, i, 9—20; compare Abstr., 1892, 633).—The author gives a new method for preparing triphenyltetrahydropyrazine by which a good yield (83 per cent.) may be obtained and the formation of diphenylpiperazine avoided. The former substance melts at 130—131°, boils above 360° under 240 mm. pressure, and crystallises in the orthorhombic system, $a:b:c = 0{\cdot}7657:1:1{\cdot}8624$; its benzene and ethereal solutions show an intense blue fluorescence. On reduction with tin and hydrochloric acid, triphenyltetrahydropyrazine yields ethylenediphenyldiamine and acetophenone; this is the result of simultaneous hydrolysis and reduction, and is the first recorded case in which the nitrogen ring has been broken, yielding the substances from which the condensation product was originally formed. Triphenyltetrahydropyrazine, dissolved in absolute alcohol, is reduced by sodium with formation of *triphenylpiperazine*, $NPh<\begin{matrix}CH_2—CH_2\\CH_2\cdot CHPh\end{matrix}>NPh$; this base is obtained in small needles melting at 101—102°, and its solution in benzene, ether, or light petroleum shows a blue fluorescence. It dissolves in mineral acids and is precipitated unchanged by water; it does not reduce metallic salts or yield definite double salts. The *picrate* forms small, yellow crystals melting at 173—175°. The *platinochloride*, $C_{22}H_{22}N_2,H_2PtCl_6$, is obtained in minute, yellow crystals which decompose at about 220°; it is insoluble in ether or water, but dissolves in alcohol. An ethereal solution of triphenylpiperazine absorbs the quantity of bromine necessary to form a mono-substitution derivative; one half of the liberated hydrogen bromide is retained by the solution. W. J. P.

Pyrazolone. By R. v. Rothenburg (*Ber.*, **26**, 868—872; compare this vol., i, 367, 368).—The preparation of pure pyrazolone from the carboxylic acid is attended with considerable difficulty owing to the smallness of the yield; it was finally obtained as a colourless oil which boils at 152—157°, and is fairly stable towards light; the darkening sometimes observed is probably due to the presence of a small quantity of impurity, which boils at 203—205°, and may consist of *dipyrazolone ketone*. The vapour density of pyrazolone, obtained by Victor Meyer's method, confirmed the formula $C_3H_4N_2O$. The derivatives have only been obtained in small quantities; *4-isonitrosopyrazolone* is a reddish-yellow oil, which crystallises in the cold, *4-azobenzenepyrazolone* is also red and has acid properties, and *4-benzalpyrazolone* has likewise a red colour. *Pyrazolonaldehyde*, $CO<\begin{matrix}NH\cdot N\\CH_2\cdot C\cdot CHO,\end{matrix}$ is obtained by distilling calcium pyrazolonecarboxylate with lime and calcium formate; it passes over as a yellow oil

which quickly crystallises, and has all the usual properties of an aldehyde.

The author has investigated the action of hydrazine hydrate on ethylic oxalodiacetate, in the hope of obtaining bispyrazolone, but the reaction proceeds in the same manner as with other orthodiketones. The ethylic oxalodiacetate, $C_2O_2(CH_2{\cdot}COOEt)_2$, was obtained from the residues from the preparation of ethylic oxalacetate, and was found by the author to crystallise from dilute alcohol in flat needles melting at 82—83°. It reacts violently with hydrazine hydrate forming ethylic β-hydrazo-β_1-ketadipate, $\begin{matrix}NH\\|\\NH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2{\cdot}COOEt\\CO{\cdot}CH_2{\cdot}COOEt\end{matrix}$, which crystallises from very dilute alcohol in brownish-yellow needles, melts at 93°, and yields hydrazine sulphate on boiling with dilute sulphuric acid.

Hydrazine hydrate acts on ethylic allylacetoacetate in the normal manner yielding 3-*methyl*-4-*allylpyrazolone*,

$$HN\!<\!\!\begin{matrix}N{=}CMe\\|\\CO{\cdot}CH{\cdot}CH_2{\cdot}CH{:}CH_2,\end{matrix}$$

which crystallises from alcohol in plates, melts at 195°, shows the characteristic reactions of the pyrazolones, and like all the 3 : 4-derivatives gives an intense reddish-brown coloration with ferric chloride. The hydrate also combines readily with ethylic acetyltrimethylenecarboxylate yielding 3-*methyl*-4-*trimethylenepyrazolone*,

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CO{-}NH\\|\\CMe{:}N\end{matrix},$$

which crystallises in almost colourless needles, melts at 195°, and gives the characteristic brown coloration with ferric chloride, but does not combine with diazobenzene chloride and nitrous acid.

H. G. C.

Synthesis of Pyrazole Derivatives by means of Ethylic Diazoacetate. By E. Buchner (*Annalen*, **273**, 214—231).—The compounds formed by the combination of ethereal salts of unsaturated acids with those of diazoacetic acid are derivatives of pyrazole. Methylic acetylenedicarboxylate, for example, combines with methylic diazoacetate forming in all probability an unstable compound of the constitution $\begin{matrix}COOMe{\cdot}C{-}CH{\cdot}COOMe\\\|\quad\quad|\\COOMe{\cdot}C{\cdot}N{:}N\end{matrix}$, which then undergoes intramolecular change into methylic pyrazoletricarboxylate,

$$\begin{matrix}COOMe{\cdot}C{=}\!=\!C{\cdot}COOMe\\|\quad\quad\times\quad\quad|\\COOMe{\cdot}C{\cdot}NH{\cdot}N\end{matrix}$$

Other acetylenic ethereal salts, methylic phenylpropiolate, for example, behave in a similar manner, but ethylenic derivatives such as the ethereal salts of acrylic, fumaric, maleic, aconitic, itaconic, citraconic, cinnamic, and benzalacetic acids yield reduction products of pyrazole or pyrazoline derivatives. Methylic fumarate and methylic diazoacetate,

for instance, may be assumed to combine to form methylic psuedo-pyrazolinetricarboxylate, $\begin{matrix}\mathrm{COOMe\cdot CH}\text{–}\mathrm{CH\cdot COOMe}\\ \quad\quad\quad\

50° or so; when a mixture of the two ethereal salts is heated immediately on the water-bath, explosive combination ensues. It crystallises well from boiling methyl alcohol and hot water, melts at 94°, and is decomposed by boiling dilute sulphuric acid with formation of carbonic anhydride and hydrazine; when treated with bromine in choroform solution, it is converted into methylic pyrazoledicarboxylate, melting at 151·5° (see below). The *silver* derivative, $C_7H_9N_2O_4Ag$, is a yellowish-brown powder.

Pyrazoline-3 : 5-dicarboxylic acid, $C_5H_6N_2O_4$, is formed when the methylic salt is hydrolysed with cold methyl alcoholic potash; it crystallises in colourless prisms, turns brown at 240°, and melts at 242°, with complete decomposition. On oxidation with sulphuric acid and freshly precipitated manganese dioxide, it yields a pyrazolecarboxylic acid, melting at 208—210°, and pyrazole-3 : 5-dicarboxylic acid. The *silver* salt is a colourless compound, stable in the light, and only sparingly soluble in boiling water. The *barium* salt and the *copper* salt are readily soluble. When the silver salt is heated in a stream of carbonic anhydride, it yields pyrazole, melting at 70° (compare Abstr., 1889, 1214).

Ethylic pyrazolinedicarboxylate, $C_9H_{14}N_2O_4$, is formed, together with ethylic iodacetate, when ethylic β-iodopropionate is heated with ethylic diazoacetate (2 mols.) at 100—110°, nitrogen being evolved; it crystallises in colourless, lustrous prisms, and melts at 99°.

F. S. K.

Pyrazoline-3 : 4 : 5-tricarboxylic acid. By E. Buchner and H. Witter (*Annalen*, **273**, 239—245; compare Abstr., 1888, 1274).—Methylic pyrazoline-3 : 4 : 5-tricarboxylate (methylic fumaricdiazoacetate), $C_9H_{12}N_2O_6$, is formed when methylic fumarate or methylic maleate is warmed with methylic diazoacetate in light petroleum solution; it separates from ether in crystals, melts at 61°, and is very readily soluble in most ordinary solvents. It is immediately oxidised by potassium permanganate in alkaline solution, and when boiled with mineral acids, it is decomposed into hydrazine, carbonic anhydride, and other compounds. The *silver* derivative is a yellowish, very unstable substance, soluble in ammonia.

Pyrazoline-3 : 4 : 5-tricarboxylic acid, $C_6H_6N_2O_6$, crystallises in almost colourless needles, has no definite melting point, and is hygroscopic and very unstable. The *barium* salt, $(C_6H_3N_2O_6)_2Ba_3$, and the *silver* salt, $C_6H_3N_2O_6Ag_3$, were prepared; the latter yields pyrazole on dry distillation. The *amide*, $C_6H_9N_5O_3$, prepared by treating the methylic salt with alcoholic ammonia, is a crystalline compound, and decomposes at about 230°. When diazoacetamide is heated with methylic fumarate at 70°, an amide of the composition

$$NH_2{\cdot}CO{\cdot}C_3N_2H_3(COOMe)_2$$

is formed; it separates from alcohol in almost colourless crystals, and melts at about 108°.

F. S. K.

Pyrazole-3 : 5-dicarboxylic acid. By E. Buchner and A. Papendieck (*Annalen*, **273**, 246—251).—*Methylic pyrazole-3 : 5-dicarboxylate*, $C_7H_8N_2O_4$, is obtained, together with methylic brom-

acetate, when methylic $\alpha\beta$-dibromopropionate is heated with methylic diazoacetate. It crystallises in lustrous plates, melts at 151·5°, gives a stable, colourless silver derivative, and is not oxidised by potassium permanganate in alkaline solution. The corresponding acid, $C_5H_4N_2O_4$, separates from hot water in crystals containing $1H_2O$, and melts at 287—290° with decomposition; it is extremely stable, and is not acted on by potassium permanganate. The acid *sodium* salt, $C_5H_3N_2O_4Na,C_5H_4N_2O_4$, is precipitated when a neutral solution of the sodium salt is treated with a solution of the acid; it crystallises with $11H_2O$, all of which are expelled at 150°. The *calcium* salt, $C_5H_2N_2O_4Ca + 5H_2O$, forms small, lustrous crystals, and loses its water at 200°. The *barium* salt, with $4H_2O$, forms lustrous prisms, and loses its water at 180°. The *silver* salt, $C_5H_2N_2O_4Ag_2$, is readily soluble in ammonia; on dry distillation, it yields pyrazole.

F. S. K.

Pyrazole-3 : 4 : 5-tricarboxylic acid. By E. Buchner and M. Fritsch (*Annalen*, **273**, 252—256).—When methylic pyrazole-3 : 4 : 5-tricarboxylate (methylic acetylenedicarboxylodiazoacetate, Abstr., 1889, 694) is treated with concentrated nitric acid, it is converted into the corresponding acid (acetylenedicarboxylodiazoacetic acid); the latter, on rapid distillation, is converted into pyrazole and *pyrazole-4-carboxylic acid*, $C_4H_4N_2O_2$, a yellowish, crystalline compound melting at 275° with decomposition.

Methylic pyrazole-3 : 4 : 5-tricarboxylate is formed, together with methylic bromacetate, by the action of methylic diazoacetate on methylic bromomaleïnate; it can also be obtained by treating the diazo-compound with methylic dibromosuccinate. F. S. K.

Preparation and Derivatives of Pyrazole. By E. Buchner and M. Fritsch (*Annalen*, **273**, 256—266; compare Abstr., 1889, 1214).—Bromopyrazole melts at 96—97°, not at 87—88°, as previously stated; its *nitrate*, $C_3H_3N_2Br,HNO_3$, separates from boiling water in crystals melting at 184—185° with decomposition; its *silver* derivative has the composition $C_3H_2N_2BrAg$.

Iodopyrazole, $C_3H_3N_2I$, prepared by treating the silver derivative of pyrazole with an ethereal solution of iodine, crystallises in colourless needles, melts at 108·5°, and forms a colourless *silver* derivative.

Nitropyrazole, $C_3H_3N_3O_2$, is formed when pyrazole is heated at 100° with a mixture of fuming nitric acid and anhydrosulphuric acid; it crystallises in colourless needles, melts at 162°, and explodes slightly when heated on platinum foil. F. S. K.

Imidazoles. By E. Bamberger (*Annalen*, **273**, 267—269).—The author regards the benzimidazoles as hexacentric compounds, and represents the nitrogen atom of the imido-group as being pentavalent, the other trivalent, as shown in the formula

According to this view, the basicity of the imidazoles is independent of the imido-group, which, being saturated, cannot form additive products with acids. The experiments described in the following papers were undertaken with the object of settling the constitution of the benzimidazoles and of elucidating their methods of formation.

F. S. K.

Constitution and Formation of Benzimidazoles. By E. BAMBERGER and J. LORENZEN (*Annalen*, **273**, 269—302; compare Abstr., 1892, 631 and 632).—The facts which point to the conclusion that the two nitrogen atoms in the benzimidazoles have different functions are the following:—Although the benzimidazoles contain two atoms of nitrogen, they form additive compounds with only one molecule of a monobasic acid and with only one molecule of an alkyl halogen compound. The imido-group has an acid character, and imparts to some benzimidazoles the character of a phenol, to others that of an acid; all secondary benzimidazoles contain one hydrogen atom which can be displaced by metals, and they are as a rule soluble in alkalis. The benzimidazoles do not yield nitroso-derivatives as would be expected if they contained an ordinary imido-group in which the nitrogen is trivalent; their acetyl derivatives are very unstable, and are quickly decomposed by boiling water. The imido-group in the glyoxalines has the same character as that in the benzimidazoles, but in the dihydroglyoxalines it has quite different functions.

Silver derivatives of the benzimidazoles, such as

$$C_6H_3Me\langle\begin{matrix}NAg\\ __\\ N\end{matrix}\rangle CMe,$$

can be prepared by treating an alcoholic solution of the base first with ammonia and then with silver nitrate; they are colourless compounds, practically insoluble in water, ammonia, and organic solvents. Of the corresponding sodium derivatives, only that of 2 : 2′-dimethylbenzimidazole was analysed; it crystallises in slender needles, and is decomposed by water, whereas the corresponding derivatives of the other benzimidazoles are stable in aqueous solution.

2 : 2′ : 3′-Trimethylbenzimidazole, $C_{10}H_{12}N_2$, is formed in small quantities when the sodium or silver derivative of 2 : 2′-dimethylbenzimidazole is treated with methylic iodide in methyl alcoholic solution, but it is best prepared from the base itself; it crystallises in lustrous prisms, melts at 141—142°, and is identical with the compound obtained by Niementowski (*Ber.*, **20**, 1878) from methylnitroparacetotoluidide, a fact which explains the mechanism of the benzimidazole formation.

2 : 2′-*Dimethyl*-3′-*benzylbenzimidazole*, $C_{16}H_{16}N_2$, prepared in a similar manner, crystallises in long, lustrous needles, and melts at 144°; the platinochloride, $(C_{16}H_{16}N_2)_2,H_2PtCl_6$, crystallises in transparent, lustrous plates.

Ethylic 2 : 2′-*dimethylbenzimidazole*-3′-*acetate*, $C_{13}H_{16}N_2O_2$, is formed when dimethylbenzimidazole is treated with sodium ethoxide and ethylic chloracetate in alcoholic solution; it crystallises in slender lustrous needles, and melts at 130·5°.

2 : 2′-*Dimethyl*-3′-*acetylbenzimidazole*, $C_{11}H_{12}N_2O$, can be obtained by heating the silver derivative with a benzene solution of acetic chloride; it crystallises in lustrous needles, melts at 241—242°, and is quickly decomposed by boiling water. The *platinochloride*, $(C_{11}H_{12}N_2O)_2,H_2PtCl_6$, crystallises in golden needles.

2 : 2′-*Dimethyl*-3′-*chlorobenzimidazole* (chlorimide), $C_9H_9N_2Cl$, is precipitated in slender needles when a saturated solution of bleaching powder is added to a well-cooled solution of 2 : 2′-dimethylbenzimidazole in dilute acetic acid; the crude product melts at 92°, and is insoluble in water. In its warm alcoholic solution, aniline produces a red coloration which changes to bluish-violet on adding hydrochloric acid; its aqueous solution oxidises quinol to quinhydrone. The moist substance slowly undergoes decomposition even in the cold, more quickly when warmed or when treated with hydrochloric acid, being partly converted into dimethylbenzimidazole with evolution of chlorine, partly into the isomeride described below.

Chloro-2 : 2′-*dimethylbenzimidazole*, $C_9H_9N_2Cl$, is best prepared by boiling the preceding compound with dry benzene, as, under these conditions, the formation of other products is almost entirely prevented; it crystallises in short, lustrous needles, melts at 223°, and is soluble in soda. The *hydrochloride*, $C_9H_9N_2Cl,HCl$, crystallises in long needles. The *platinochloride*, $(C_9H_9N_2Cl)_2,H_2PtCl_6$, forms golden needles, and is sparingly soluble in water. The *picrate*, *ferrocyanide*, and *nitrate* are crystalline, sparingly soluble compounds. The *silver* derivative has the composition $C_9H_8N_2ClAg$.

Chloro-2 : 2′-*dimethylchlorobenzimidazole* (chlorochlorimide),

$$C_9H_8N_2Cl_2,$$

is precipitated in yellowish needles when the preceding compound is treated with bleaching powder under the conditions already described, the hydrogen of the imido-group being substituted; the crude product melts at 85°, but after recrystallisation from alcohol and water at 103—105°. It is moderately stable when dry, but the moist substance undergoes decomposition at the ordinary temperature with evolution of chlorine, especially when treated with hydrochloric acid; when boiled with dry benzene, it seems to yield a mixture of chlorodimethylbenzimidazole (m. p. 223°), a dichlorinated derivative, $C_9H_8N_2Cl_2$, melting at 238°, and a trichlorinated derivative melting at about 285°.

Dichloro-2 : 2′-*dimethylchlorobenzimidazole* (dichlorochlorimide) is formed when the dichloro-compound melting at 238° is treated with bleaching powder solution; the crude product melts at 120° with decomposition, is decomposed by acids with evolution of chlorine, and undergoes intramolecular change into the trichloro-compound described below when boiled with alcoholic benzene.

Trichloro-2 : 2′-*dimethylbenzimidazole*, $C_9H_7N_2Cl_3$, is best prepared by treating dimethylbenzimidazole with bleaching powder in boiling hydrochloric acid solution; it is soluble in acids and alkalis, and its solution in alcoholic ammonia gives with silver nitrate a colourless, amorphous precipitate of the composition $C_9H_6N_2Cl_3Ag$. The *hydrochloride*, $C_9H_7N_2Cl_3,HCl$, crystallises in lustrous plates; the *platino-*

chloride, $(C_9H_7N_2Cl_3)_2,H_2PtCl_6$, in long needles; the *nitrate* and the *sulphate* are also crystalline.

These salts are decomposed by water, being converted into transparent gelatinous masses, but, on heating gently, the base separates in small, lustrous prisms.

Trichloro-2 : 2′-*dimethylchlorobenzimidazole*, $C_9H_6N_2Cl_4$, is formed when the preceding compound is treated with bleaching powder in cold dilute hydrochloric acid solution; it is a crystalline powder, does not melt at 310°, and is decomposed by water, alcohol, and mineral acids with evolution of chlorine, being reconverted into the trichloro-compound.

The amidines resemble the benzimidazoles in constitution, and, like the latter, they have the property of forming silver derivatives; the compound, $C_{14}H_{12}N_2Ag$, prepared from ethenyldiphenylamidine is insoluble in water, ammonia, and alcohol, and is not decomposed by boiling with water or hot dilute alcohol, whereas with boiling absolute alcohol it gives a silver mirror. Ethenyldiphenylamidine resembles the 2-methylbenzimidazole derivative in combining with phthalic anhydride to form a yellow, crystalline dye, which, however, could not be separated from the phthalanil produced at the same time; methenyldiphenylamidine, on the other hand, does not yield a trace of a yellow compound when heated with phthalic anhydride.

F. S. K.

Behaviour of the 2′-Methyl Group in Benzimidazoles. By E. Bamberger and B. Berlé (*Annalen*, **273**, 303—342; compare Abstr., 1892, 631 and 632).—*Benzylidenedimethylbenzimidazole*,

$$C_6H_3Me\!<\!\overset{NH}{\underset{N}{}}\!>\!C\cdot CH{:}CHPh,$$

is formed when 2 : 2′-dimethylbenzimidazole is heated with benzaldehyde at 200°; it is a colourless, flocculent substance, sinters at about 100°, and melts at about 120° with effervescence. The *hydrochloride*, $C_{16}H_{14}N_2,HCl$, crystallises in colourless needles, melts at 283—284°, and is readily soluble in alcohol, but very sparingly in water; the anhydrous salt is hygroscopic. The *platinochloride*, $(C_{16}H_{14}N_2)_2,H_2PtCl_6$, is a yellow, crystalline powder. The *dibromide* crystallises in yellowish needles, and has no definite melting point.

The *phthalone*, $C_{17}H_{12}N_2O_2$, prepared by heating 2 : 2′-dimethylbenzimidazole with phthalic anhydride at 200°, crystallises in yellow, rectangular, microscopic plates, and does not melt at 330°; it sublimes in yellow needles, dissolves in concentrated sulphuric acid with a violet coloration, and turns red when treated with soda, owing to the formation of a sodium derivative.

The *phthalone* $C_{17}H_{10}N_2O_4$, obtained from 2′-methylbenzimidazole-2-carboxylic acid under like conditions, resembles the preceding compound, and dissolves in concentrated sulphuric acid with a wine-red coloration.

The *phthalone* $C_{16}H_{10}N_2O_2$, derived from 2-methylbenzimidazole, separates from glacial acetic acid in a yellow, flocculent condition, but is dirty green when dry; it melts at 223—225° with previous

softening, is more readily soluble than the 2′-phthalones, and dissolves in concentrated sulphuric acid with a dark yellow coloration.

2′-Methylbenzimidazole-2-carboxylic acid, $C_9H_8N_2O_2$, is formed, together with traces of the dicarboxylic acid and oxalic acid, when 2 : 2′-dimethylbenzimidazole is warmed with potassium permanganate; it crystallises in colourless needles, melts at 305° with decomposition when quickly heated, and is almost insoluble in all ordinary solvents except glacial acetic acid and boiling water. It has only feeble acid properties, measurements of its electrical conductivity showing it to be 60 times weaker than benzoic acid and 5 times weaker than pyridineorthocarboxylic acid; its alkali salts are decomposed by acetic acid, its barium salt by carbonic acid. The *silver* salt, $C_8H_7N_2{\cdot}COOAg$, is a colourless, voluminous compound, soluble in ammonia. The *copper* salt is crystalline and insoluble in water, but the *barium* salt and the alkali salts are readily soluble. The *nitrate*, $C_9H_8N_2O_2,HNO_3$, crystallises in small, lustrous needles, decomposes at 220—230°, and is sparingly soluble in cold water. The *hydrochloride*, $C_9H_8N_2O_2,HCl$, crystallises in needles melting at 317—318°; the *platinochloride* forms lustrous, orange prisms which contain $2H_2O$, the anhydrous salt being hygroscopic. When the acid is heated with soda-lime, it is converted into 2′-methylbenzimidazole.

Benzimidazole-2-carboxylic acid, $C_8H_6N_2O_2$, prepared by oxidising 2-methylbenzimidazole, crystallises in microscopic prisms, does not melt at 320°, and is insoluble or nearly so in all ordinary solvents except glacial acetic acid and alcohol. The *platinochloride* forms yellow, prismatic crystals, and, like the *nitrate*, is only sparingly soluble in cold water. The *copper* and *lead* salts are crystalline, but the *silver* salt is amorphous.

2-Methylbenzimidazole-2′-carboxylic acid, $C_9H_8N_2O_2 + \frac{1}{2}H_2O$, can be obtained by oxidising the benzylidene derivative of dimethylbenzimidazole (see above) with potassium permanganate; it crystallises in colourless, lustrous needles, and when heated very quickly, melts at 157·5° with evolution of carbonic anhydride. It has feeble basic properties and dissolves in mineral acids, but is reprecipitated on adding sodium acetate; its acid character, however, is strongly marked. The *silver* salt, $C_9H_7N_2O_2Ag$, is not appreciably soluble in boiling water; in aqueous solutions of the acid, ferrous sulphate produces a straw-yellow coloration. When the acid is distilled or boiled with glacial acetic acid, it is decomposed into carbonic anhydride and 2-methylbenzimidazole.

Benzimidazole-2 : 2′-dicarboxylic acid is produced when 2′-methylbenzimidazole-2-carboxylic acid is boiled with potassium permanganate, but oxidation takes place very slowly; the acid was isolated in the form of its *platinochloride*, $(C_9H_6N_2O_4)_2,H_2PtCl_6$, a reddish-yellow, crystalline compound sparingly soluble in cold water.

Nitrobenzimidazole, $NO_2{\cdot}C_6H_3{<}^{NH}_{N}{>}CH$, prepared by treating benzimidazole with a mixture of nitric and sulphuric acids below 30°, crystallises in microscopic needles, and melts at 203°; it dissolves freely in acids, alkalis, and alkali carbonates. The *nitrate* crystallises in microscopic needles, and melts at about 210—215° when slowly

heated. The reduction product of the nitro-compound is very unstable. F. S. K.

Opening the Benzimidazole Ring. By E. Bamberger and B. Berlé (*Annalen*, **273**, 342—363; compare Abstr., 1892, 631, 632).—When benzimidazole is dissolved in dilute soda and benzoic chloride gradually added to the ice-cold solution, orthodibenzoylphenylenediamine separates in crystals and formic acid remains in solution; this decomposition takes place quantitatively. When orthodibenzoylphenylenediamine is heated at a temperature above its melting point, it is decomposed into 2′-phenylbenzimidazole, melting at 282°, and benzoic acid; the platinochloride of this imidazole contains 3 mols. H_2O when dried at 120° or over sulphuric acid.

2′-Methylbenzimidazole is decomposed by soda and benzoic chloride into orthodibenzoylphenylenediamine and acetic acid, whereas 2-methylbenzimidazole yields dibenzoyltoluylenediamine [Me : $NHBz_2$)$_2$ = 1 : 3 : 4].

Nitrorthodibenzoylphenylenediamine, $NO_2{\cdot}C_6H_3(NHBz)_2$, prepared by treating nitrobenzimidazole (compare preceding abstract) with benzoic chloride and soda, crystallises in lustrous needles, melts at 235—236°, and gives an intense yellowish-red coloration with potash, owing to the formation of a salt, which, however, is decomposed by water.

α-Dibenzoyldiamidoethylene, $C_2H_4(NHBz)_2$, is formed, together with traces of the β-compound, when glyoxaline is treated with soda and benzoic chloride in the cold. It crystallises from boiling alcohol in transparent, colourless, monoclinic prisms, $a : b : c = 0{\cdot}5215 : 1 : ?$, $\beta = 83° 41'$, melts at 202—203°, and dissolves freely in most organic solvents, and in concentrated mineral acids. Molecular weight determinations by the boiling point method, chloroform being used, gave results agreeing well with the theoretical.

β-Dibenzoyldiamidoethylene, $C_2H_4(NHBz)_2$, is formed when the α-compound is heated with acetic acid. It crystallises from boiling alcohol in small, lustrous needles, decomposes at 280—290°, and is much more sparingly soluble in the ordinary organic solvents and in hydrochloric acid than the α-compound just described. Both compounds are rather quickly decomposed by boiling glacial acetic acid, yielding brown products, the nature of which has not yet been determined, but they are not decomposed by boiling alcoholic potash; their isomerism is probably stereochemical and comparable with that of maleïc and fumaric acids.

3′-*Benzoylbenzimidazole*, $C_{14}H_{16}N_2O$, can be obtained by warming benzimidazole with benzoic chloride. It crystallises in slender needles or plates, melts at 91—92°, and is readily decomposed by boiling water and by cold mineral acids into benzimidazole and benzoic acid; when treated with 10 per cent. potash at the ordinary temperature, it does not yield formylbenzoylphenylenediamine, as might have been expected, but is converted into benzoic acid, benzimidazole, and a compound melting at 134—135°, the nature of which was not ascertained. F. S. K.

Addition of Chloral to Quinoline Bases and Benzimidazoles. By E. Bamberger and B. Berlé (*Annalen*, **273**, 364—373).—Paratoluquinoline combines readily with chloral, forming a compound of the composition $C_{10}NH_9,C_2HCl_3O + H_2O$; this crystallises in transparent prisms, melts at 79°, previously softening, and is decomposed into its components when kept over sulphuric acid under reduced pressure or when boiled with water. Paratoluquinoline also combines with anhydrous zinc chloride, forming a crystalline compound which melts at 229° and has the composition $(C_{10}NH_9)_2,ZnCl_2$.

A compound of the composition C_9NH_7,C_2HCl_3O is formed when quinoline is mixed with chloral; it crystallises in lustrous prisms, and melts at 63—65°.

2 : 2′-Dimethylbenzimidazole combines with chloral even in the cold, yielding a colourless, crystalline substance of the composition $C_{11}H_9N_2Cl_3$, which contains $1\frac{1}{2}$ or $2H_2O$; it has no definite melting point, and is decomposed by boiling water.

The compound obtained by the combination of benzimidazole and chloral is a colourless, granular substance, which melts at 122—131° with decomposition, and has the composition $C_7H_6N_2,C_2HCl_3O + H_2O$.

F. S. K.

Formula of Glyoxaline. By A. Wohl and W. Marckwald (*Ber.*, **26**, 973—975).—The authors (Abstr., 1888, 624, 866) proved the correctness of Japp's formula long before Bamberger (Abstr., 1892, 632). They now defend the validity of their proof against his recent remarks (this vol., i, 432, *et seq.*).

C. F. B.

Formation of Dihydroquinazolines: a New Example of Intramolecular Transposition. By O. Widman (*J. pr. Chem.* [2], **47**, 343—366; compare Abstr., 1890, 1258).—*Orthonitrobenzylparabromaniline*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Br$, is made by heating orthonitrobenzylic chloride (1 part) with parabromaniline (4 parts) for three-quarters of an hour on the water-bath. It crystallises in yellow, vitreous prisms or long, four-sided tables, and melts at 84—85°. Its crystallography is detailed. The *acetyl* derivative,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NAc\cdot C_6H_4Br,$$

crystallises in white, rhombic, or six-sided tables, melts at 137—138°, and is nearly insoluble in ether and only sparingly soluble in hot alcohol.

Orthamidobenzylacetanilide was described by Paal and Krecke (Abstr., 1892, 80) as being obtained when orthonitrobenzylacetanilide is reduced by tin and hydrochloric acid, but not when zinc and glacial acetic acid are used; they give its melting point as 126—127°. The author reduced the nitro-derivative with zinc and hydrochloric acid in alcohol, and with zinc and glacial acetic acid, and in both cases obtained a product which is undoubtedly orthamidobenzylacetanilide; it crystallises in small, colourless tables and in an ill-defined form, and melts at 80—81°. When heated with acetic anhydride, it yields orthacetamidobenzylacetanilide (m. p. 121°;

Paal and Krecke, *loc. cit.*), whereas the methylphenyldihydroquinazoline (Paal and Krecke, Abstr., 1890, 1443) remains unchanged. When heated with hydrochloric acid, it is converted into *orthamidobenzylaniline dihydrochloride*, which crystallises in rectangular tables, melts at 183—185°, and dissolves easily in water.

Orthamidobenzylacetoparabromaniline is obtained by reducing the nitro-derivative (see above) with zinc in glacial acetic acid; it crystallises in colourless tables, and melts at 106—107°. Its crystallography is given.

The author concludes that the obtaining of Paal and Krecke's methylphenyldihydroquinazoline (*loc. cit.*) is not an accident of reduction.

The crystallography of orthamidobenzylacetoparatoluidide,

$$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NAc{\cdot}C_6H_4Me$$

(Abstr., 1890, 1258), is given. When its solution in dilute hydrochloric acid is allowed to remain at the ordinary temperature for a week, it undergoes intramolecular transposition, and is converted into *orthacetamidobenzylparatoluidine*, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me$; this crystallises in long needles, melts at 141°, and dissolves easily in hot alcohol and chloroform, but only sparingly in ether, light petroleum, or cold alcohol. Hydrolysis by hydrochloric acid converts it into orthamidobenzylparatoluidine. When treated with sodium nitrite and hydrochloric acid, it yields *acetamidobenzylnitrosoparatoluidine*, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(NO){\cdot}C_6H_4Me$, which crystallises in pale yellow needles, and melts at 115—116°.

Orthacetamidobenzylaniline, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, is the product of a similar intramolecular transposition of orthamidobenzylacetanilide in hydrochloric acid. It crystallises in brittle prisms, melts at 125°, and is undoubtedly identical with the compound described by Paal and Krecke as orthamidobenzylacetanilide (Abstr., 1892, 80). The *hydrochloride* crystallises in tables or prisms, and melts at 180°; its solutions become green in air. The *chromate* crystallises in slender, yellow needles, very sparingly soluble in cold water. The *nitroso-derivative*, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPh{\cdot}NO$, crystallises in colourless needles, and melts at 112—113°. The author is of opinion that the substance (m. p. 178°) obtained by Paal and Krecke (*loc. cit.*) by oxidising orthacetamidobenzylaniline by potassium permanganate is orthacetamidobenzoic acid.

Orthacetamidobenzylparabromaniline, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Br$, is the transposition product of orthamidobenzylacetoparabromanilide, and is similarly prepared; it crystallises in prisms, and melts at 148—149°.

When orthamidobenzylacetanilide is heated with dilute hydrochloric acid and alcohol in a reflux apparatus, the hydrochloride of 2-methyl-3-phenyldihydroquinazoline (with $2H_2O$) is obtained; this melts at 263°, and agrees in properties with the hydrochloride of the base obtained by Paal and Krecke (Abstr., 1890, 1443) by reducing orthonitrobenzylacetanilide with tin and hydrochloric acid. The free base crystallises in thin laminæ, and melts at 80°. The stannochloride forms white needles, and melts at 122—123°.

2-*Methyl*-3-*paratolyldihydroquinazoline*, $C_6H_4<\begin{matrix}N=C\cdot Me\\ CH_2\cdot N\cdot C_6H_4Me\end{matrix}$, is obtained when orthamidobenzylacetoparatoluidide is heated with hydrochloric acid in a similar manner; it crystallises in white tables, and melts at 104—106°. The *stannochloride* crystallises in long, white needles, and melts at 139—140°.

2-*Methyl*-3-*parabromophenyldihydroquinazoline*,

$$C_6H_4<\begin{matrix}N=C\cdot Me\\ CH_2\cdot N\cdot C_6H_4Br\end{matrix}$$

is similarly prepared from orthamidobenzylacetobromanilide; it crystallises in long needles, and dissolves easily in alcohol; the *hydrochloride* is sparingly soluble.

When these three "anhydro-bases" are boiled with such solvents as benzene and light petroleum, they are decomposed; thus, in the case of the phenyl derivative, a white powder separates, which melts at 89° and dissolves in alcohol, the solution giving a precipitate with water which is yet a third substance, for it melts at 140°. So also the bromophenyl derivative yields a powder which melts at 110°, dissolves in glacial acetic acid, and, on dilution, yields crystals which melt at 168—169°.

The above researches show that Paal and Krecke failed to differentiate between the reduction products of orthonitrobenzylacetanilide and the transposition and condensation products of the action of hydrochloric acid on the amido-derivative obtained by the reduction (*loc. cit.*). Another correction has to be made in the statements of these authors; they obtained 2-methyl-3-phenyldihydroquinazoline by distilling orthamidobenzylacetanilide. Now it has been shown above that the compound which they thus named is, in reality, orthacetamidobenzylaniline, which undoubtedly would yield the quinazoline when distilled, for the present author has distilled orthacetamidobenzyltoluidine and obtained the corresponding quinazoline; he has, however, failed to obtain quinazolines by distilling orthamidobenzylacetanilide and orthamidobenzylacetoparatoluidide.

A. G. B.

Tetrazole Derivatives from Diazotetrazotic acid. By J. Thiele and J. T. Marais (*Annalen*, **273**, 144—160; compare Abstr., 1892, 1295).—When a dilute (about 2 per cent.) solution of amidotetrazotic acid is diazotised with hydrochloric acid and sodium nitrite, the solution of diazotetrazole does not explode at ordinary temperatures, but decomposes quietly when boiled, with evolution of nitrogen and cyanogen; quantitative experiments showed that about 95 per cent. of the diazotetrazole is decomposed, in accordance with the equation $2CN_6 = C_2N_2 + 5N_2$, the remainder being probably converted into hydroxytetrazole and nitrogen, $CN_6 + H_2O = CH_2N_4O + N_2$. Assuming that diazotetrazole, like the diazobenzenesulphonic acids, exists in solution as an inner anhydride, its constitution may be expressed by the formula $N<\begin{matrix}N:C-N\\ N\cdot N=N\end{matrix}$.

Sodium diazotetrazotate, $N\lessgtr^{N\cdot N}_{NNa}\gtrdot C\cdot N{:}N\cdot ONa$, is formed when an aqueous solution of diazotetrazotic acid is neutralised with soda; as the salt is extremely soluble in water but insoluble in all other liquids, very special precautions have to be taken in order to obtain it in a pure condition. It is precipitated from its aqueous solution in colourless needles on the addition of alcohol; its solution has a strongly alkaline reaction, and only slowly undergoes decomposition when boiled, provided that carbonic anhydride be excluded. The dry salt decomposes suddenly, but not explosively, when heated, and is decomposed by concentrated sulphuric acid with production of flame. The *barium* salt was obtained, in an impure condition, as a yellow powder, readily soluble in water with alkaline reaction; its aqueous solution gives a precipitate of tetrazoleazo-β-naphthylamine (*loc. cit.*) on treatment with β-naphthylamine and acetic acid.

A *sodium* compound of the composition $C_2N_{10}ONa_2 + 5H_2O$ is obtained in yellow plates when a moderately concentrated solution of sodium diazotetrazotate is boiled for a long time and then cooled; apparently the same compound is formed when carbonic anhydride is passed into a boiling solution of the diazo-salt, but in both cases the yield is small. The dry substance explodes with great violence when heated at about 170°, and its aqueous solution gradually undergoes decomposition on boiling, with evolution of gas; in its aqueous solution, many metallic salts produce crystalline or amorphous precipitates, but β-naphthylamine gives no reaction. The constitution of the compound is possibly represented by the formula

$$N\lessgtr^{NNa}_{N\cdot N}\gtrdot C\cdot N{:}N\cdot N\lessgtr^{N{:}N\cdot N}_{C(ONa)}\gtrdot,$$

that is to say, it is possibly a sodium derivative of hydroxyazotetrazole; the fact that, though highly coloured, it is converted into a colourless substance on treatment with reducing agents supports this view. The corresponding *barium* derivative, $C_2N_{10}OBa + 4H_2O$, is comparatively sparingly soluble in water, from which it crystallises in small, yellow needles; it is highly explosive.

Benzaltetrazylhydrazine, $CN_4H\cdot NH\cdot N{:}CHPh$, is formed when a dilute solution of diazotetrazole is poured into a well-cooled mixture of stannous chloride and concentrated hydrochloric acid, and the solution then treated with benzaldehyde. It crystallises in lustrous needles, melts at 235°, and has moderately strong acid properties, dissolving freely in ammonia and alkali carbonates. The *sodium* derivative, $C_8H_7N_6Na + 3H_2O$, crystallises in prisms, and is readily soluble in water. The *calcium* derivative, $(C_8H_7N_6)_2Ca$, and the *barium* derivative crystallise with $6H_2O$, and effloresce on exposure to the air.

Tetrazylhydrazine, $N\lessgtr^{N\cdot N}_{NH}\gtrdot C\cdot NH\cdot NH_2$, can be prepared by boiling the benzal derivative with 25 per cent. hydrochloric acid, and then decomposing the hydrochloride which is formed with sodium acetate in an atmosphere of carbonic anhydride. It forms yellowish, crystalline aggregates, melts at 199° with decomposition, and is in-

soluble in alcohol and ether; it is very readily oxidised, its aqueous solution turning red on exposure to the air or on the addition of a trace of ferric chloride. It has a strongly acid reaction, dissolves readily in alkalis and ammonia, and forms a colourless, insoluble silver derivative and a green copper derivative; it also forms moderately stable salts with acids. The *hydrochloride*, $CN_6H_4,2HCl$, crystallises in colourless needles, and melts at 176°; its aqueous solution undergoes partial dissociation on evaporation at 100°.

Methyltetrazylpyrazolone, $\begin{matrix}CH{-}CO\\ \|\\ CMe{\cdot}NH\end{matrix}\!>\!N{\cdot}C\!<\!\begin{matrix}N{-}N\\ \|\\ NH{\cdot}N\end{matrix}$, is produced when tetrazylhydrazine is boiled with excess of ethylic acetoacetate. It crystallises from hot water in colourless needles, and melts at 215° with decomposition; it has an acid reaction, gives an intense yellow coloration with sodium nitrate, and with ferric chloride a brownish-violet coloration which becomes violet on diluting largely, brownish-yellow on adding acids. F. S. K.

A Homologue of Coniïne. By F. Jacobi and C. Stoehr (*Ber.*, **26**, 949—951).—When α-isobutylenepyridine (Abstr., 1891, 81) is reduced with sodium ethoxide, it yields a *methylconiïne*,

$$CH_2\!<\!\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}NH\end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CHMe.$$

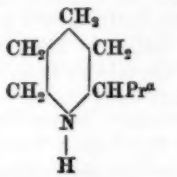
The pure base is a colourless liquid of sp. gr. 0°/4° = 0·8583. It has the same odour and solubility as coniïne, boils at 181—182° (mercurial thread entirely in the vapour), and is volatile with steam. The *hydrochloride* forms colourless needles, and melts at 194—195°; the *platinochloride* melts at 186—187° with decomposition; the *hydriodide* crystallises in long needles or prisms, and melts at 208—209°; whilst the *cadmioiodide* crystallises in monosymmetric prisms, and melts at 131—132°. A. R. L.

Isoconiïne and the Asymmetrical Nitrogen Atom. By A. Ladenburg (*Ber.*, **26**, 854—865).—When dry coniïne hydrochloride is distilled with one-fourth its weight of zinc-dust, it yields, in addition to conyrine and unaltered coniïne, a quantity of a new base isomeric with the latter, for which the author proposes the name *isoconiïne*. It is separated from coniïne by treating the mixed platinochlorides with alcohol and ether, which dissolves the coniïne platinochloride, leaving the isoconiïne salt as a residue, from which the free base may be obtained in the usual manner. In most of its properties, isoconiïne closely resembles coniïne; it has almost the same boiling point and specific gravity, and its hydrochloride melts at the same temperature. The platinochlorides, however, differ considerably, that of isoconiïne being, as already stated, insoluble in alcoholic ether; it is dimorphous, crystallising in rhombic prisms, $a:b:c = 0{\cdot}6955:1:0{\cdot}3818$, melting at 172—175°, and in monosymmetric crystals melting at 160°. It rotates the plane of polarised light to the right, but to a less extent than coniïne, $[\alpha]_D$ being 8·19 and 13·79 in the two cases. It might therefore be supposed that isoconiïne is a mixture of dextro- and inactive coniïne, but this view cannot be correct, as the base, even

when prepared in a varying manner, has always the same rotatory power. Moreover, it is not formed by distilling inactive coniïne with zinc-dust, and the specific rotatory powers of benzoylconiïne and benzoylisoconiïne, although different, do not stand to one another in the same ratio as those of the free bases, which would be the case if the substance were a mixture of dextro- and inactive coniïne.

In order to ascertain whether the isomeride was formed from coniïne by the conversion of the propyl into the isopropyl group, it was distilled with an excess of zinc-dust; the product was, however, found to be identical with the base obtained in a similar manner from coniïne. Hence isoconiïne also contains the propyl group, and is structurally identical with coniïne, the two compounds being, therefore, stereometrical isomerides.

To account for the existence of such isomerides in piperidine derivatives, the author propounds a hypothesis according to which the valencies of nitrogen atom in piperidine and compounds containing similar nuclei do not all lie in the same plane, and suggests that the isomerism now under consideration is caused by the position of this valency relatively to the other groups in the molecule. Thus, in the present case two isomerides would be possible, according as the third valency of the nitrogen atom is on the same side or on the opposite side to the propyl group. It is also possible to explain the existence of the two isomerides if the valencies of the nitrogen atom all lie in the same plane, the third valency being in the one case inside, and in the other outside, the ring, as shown in the following formulæ.



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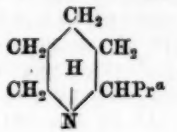

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Further investigations are in progress to ascertain if similar isomerides can be prepared from other piperidine derivatives. Results have been obtained in the case of dextro-α-pipecoline which appear to be analogous to those obtained with dextro-coniïne. H. G. C.

Nicotine. By A. Pinner (*Ber.*, **26**, 765—771).—The author replies to a recent paper by Blau (this vol., i, 375). By the interaction of nitrosohexahydronicotine, $C_{10}H_{18}N_2(NO)_2 + \frac{1}{2}H_2O$, and phenylsulphonic chloride, *phenylsulphonehexahydronicotine*,

$$C_{10}H_{18}N_2(SO_2Ph)_2,$$

is formed. It crystallises from alcohol, melts at 133—134°, and is insoluble in alkali, thus proving that hexahydronicotine contains two imido-groups. Hexahydronicotine, which was the sole product obtained by the reduction of nicotine with sodium amalgam, yields two bromo-additive products; these are being further investigated, the one, $C_{10}H_{20}N_2,2HBr_3$, is red and unstable, the second, $C_{10}H_{20}N_2HBr,HBr_3$, is yellow.

The author has already described the action of hydrochloric acid on dibromocotinine (this vol., i, 286). After treating the product with mercuric chloride and removing the mercury, two compounds can be precipitated by potassium carbonate; the more sparingly soluble substance, which it is proposed to term *apocotinine*, $C_9H_9NO_3$, crystallises from water in yellow plates, melts at 160°, and forms salts with acids and bases. The *copper salt*, $(C_9H_9NO_3)_2Cu + H_2O$, is crystalline. The second compound precipitated by potassium carbonate is *bromocotinine*, $C_9H_{11}BrN_2O$; it crystallises from water in long, colourless needles, melts at 120°, and undergoes decomposition at higher temperatures. Most of the salts of this base are readily soluble.

Cotinine, $C_{10}H_{12}N_2O$, is easily reduced by means of sodium in alcoholic solution, ammonia being eliminated; the remaining reduction products are being investigated. J. B. T.

Decomposition of Salts of Nicotine and the Action of Alcohol on them. By R. Nasini and A. Pezzolato (*Gazzetta*, **23**, i, 43—58; compare Abstr., 1891, 771).—The electrical conductivity of nicotine in aqueous solution is less than that of ammonia, and increases with dilution just as in the case of that base; that nicotine is a feeble base is also shown by the fact that dilute aqueous solutions, containing the alkaloïd and hydrochloric or acetic acid in molecular proportion, exhibit a contraction on mixing, instead of the augmentation of volume noticed with strong bases and acids. Even when pure nicotine and pure liquid acetic acid are mixed in molecular proportion, a contraction of about 2·5 per cent. in volume occurs. The rotatory power of this mixture of the base with acetic acid at 20° is $[\alpha]_D = -72{\cdot}21°$, a number of opposite sense to that assigned by Schwebel (Abstr., 1883, 354) to nicotine acetate in aqueous solution. The specific rotation in aqueous solution is $[\alpha]_D = +49{\cdot}68°$; on adding water to the lævorotatory anhydrous acetate, the rotation gradually decreases until, when 5 mols. H_2O have been added for every molecule of the salt, the solution becomes dextrorotatory; Schwebel's formula for the rotation, however, holds fairly well even for a solution containing 65 per cent. of the acetate. Alcoholic solutions of the salt are always lævorotatory, $[\alpha]_D = -59°$ to $-65°$, and on adding alcohol to dilute aqueous solutions the dextro-rotation is lessened. The addition of the corresponding quantity of triethylamine to an alcoholic solution of nicotine acetate completely decomposes the salt, for the specific rotation of the nicotine present then assumes the same value as that of nicotine itself in alcoholic solution. Complete decomposition of the salt does not occur on adding aniline or ammonia; boric acid slightly lowers the specific rotation of nicotine in alcoholic solution.

Much the same behaviour is noticed with the sulphate and hydrochloride as with the acetate; aqueous solutions of these salts are dextrorotatory, whilst alcoholic solutions are strongly lævorotatory. Polarimetric measurements made on the acetate in benzene solution show that the lævo-rotation is about the same as in alcoholic solutions; cryoscopic determinations in benzene solution give a molecular depression indicating the existence of the salt as such.

The authors conclude that nicotine has much more pronounced basic properties in aqueous solutions than in alcoholic; this is confirmed by the observation that the salts of this alkaloïd are more readily decomposed by stronger bases in alcoholic than in aqueous solutions. The fact that nicotine and similar alkaloïds (compare Menschutkin, Abstr., 1883, 708) are more strongly basic in aqueous solution is satisfactorily explained by assuming the formation of hydrates; on the addition of acids to such aqueous solutions, salts of the more active hydrated base are formed, whilst the slight stability of the salts, when dissolved in other solvents, is due to their being compounds of the more feeble anhydrous base. W. J. P.

Amides of Ecgonine. By A. Einhorn and F. K. de Norwall (*Ber.*, **26**, 962—973; compare this vol., i, 378).—Aqueous ammonia merely hydrolyses the methylic salt of ecgonine. Alcoholic ammonia, however, at 100°, converts the *l*-salts into *l-ecgonineamide*,

$$OH\cdot C_7NH_{10}Me\cdot CONH_2,$$

which melts at 198°, and forms lustrous, rhombic prisms or needles, $a : b : c = 0{\cdot}7199 : 1 : 0{\cdot}5459$. Curiously enough, the *r*-methylic salt is by this treatment converted into the ethylic salt; with methyl-alcoholic ammonia, however, at 150°, it yields *r-ecgonineamide*, which melts at 173°, and forms large crystals, or a felted mass of small needles. The following salts were prepared:—Of *l*-ecgonineamide: the *hydrochloride*, $C_9H_{16}N_2O_2,HCl$, white needles melting with decomposition at 275°; the *aurochloride*, $C_9H_{16}N_2O_2,AuCl_4 + 1\frac{1}{2}H_2O$, yellowish needles melting at 70—80°, when anhydrous at 140—142°; the *platinochloride*, $(C_9H_{16}N_2O_2)_2.H_2PtCl_6$, orange plates melting with decomposition at 239°; the *hydrobromide*, with H_2O, large prisms melting with decomposition at about 260°; the *hydriodide*, with H_2O, monoclinic plates, or staurolitic twins, melting at 245°; the *picrate*, with H_2O, needles melting at 150°. Of *r*-ecgonineamide: the *hydrochloride*, large prisms melting at 268°; the *picrate*, needles melting at 177°. Both amides, when heated at 95° with alcoholic methylic iodide, yield *methiodides*, $C_{10}H_{19}N_2O_2I$; the *l*-variety forms tables or needles melting at 203°, the *r*-variety, with H_2O, plates melting at 220°; along with the former a second iodo-compound, melting at 223°, was obtained.

Benzoic chloride by itself has no action on ecgonineamide when the two are taken in molecular proportion. If excess of benzoic chloride is used at 100°, the *l*-amide yields *l-ecgoninenitrile*,

$$OH\cdot C_7NH_{10}Me\cdot CN,$$

as needles melting at 145·5°; *hydrochloride*, $C_9H_{19}N_2O,HCl$, forms small lustrous plates. The *r*-amide under these conditions yields *benzoyl-r-ecgoninenitrile*, $OBz\cdot C_7NH_{10}Me\cdot CN$, as very soluble crystals; the *hydrobromide*, $C_{16}H_{18}N_2O_2,HBr$, needles melting at 210°; the *platinochloride*, $(C_{16}H_{18}N_2O_2)_2.H_2PtCl_6$, flesh-coloured needles; the *picrate*, needles melting at 227°. The corresponding *benzoyl-l-ecgoninenitrile* was obtained from the *l*-nitrile with benzoic chloride in ethylic acetate solution, and also directly from the *l* amide by the action of benzoic

at 105°; in the presence of soda; it forms fern-like crystals melting. chloride the *hydrochloride*, + HCl, white plates or lustrous prisms *Acetyl-r-ecgonine*, $OAc{\cdot}C_7NH_{10}{\cdot}CN$, was obtained as an oil by boiling the *r*-amide with acetic anhydride; its *hydriodide*, $C_{11}H_{16}N_2O_2,HI$, forms white needles with satiny lustre melting with decomposition at 243°.

C. F. B.

Hygrineoxime. By C. Liebermann and O. Kühling (*Ber.*, **26**, 851—852).—This substance, $C_5H_{15}N{:}NOH$, obtained from "low-boiling hygrine," $C_5H_{15}NO$, and hydroxylamine, forms white crystals melting at 116—120°; its formation shows that the oxygen in hygrine must be in the carbonyl condition. It forms no definite compound with platinum, gold, or mercuric chlorides, or with potassium mercuriodide, but it yields a *picrate*, $C_8H_{16}N_2O,C_6H_3N_3O_7$, as needles melting at 160°, and, when boiled with methyl alcohol and methylic iodide, yields *methylhygrineoxime hydriodide*, $C_5H_{15}MeN_2O,HI$, as white needles.

C. F. B.

Alkaloïds of Corydalis nobilis. By E. Birsmann (*Chem. Centr.*, 1893, i, 35; from *Inaug. Diss*, *Dorpat*, 1892).—The plant and root were extracted with dilute alcohol, the alcohol evaporated, the residue acidified and washed with light petroleum. The liquid is then extracted with benzene (1), the aqueous solution supersaturated with sodium carbonate, when a brown resin (2) separates, and the alkaline solution extracted with chloroform (3). The benzene extract (1) is treated with a little strong alcohol to precipitate tannin, then treated with very dilute hydrochloric acid, and the acid extract precipitated with soda. After recrystallisation, an alkaloïd, $C_{21}H_{21}NO_4$, is obtained, which melts at 128°, has $[\alpha]_D = +276{\cdot}6°$, and is soluble in chloroform and benzene. From the resin (2), by purification with alcohol and crystallisation from much water, *corydalinobiline*, $C_{22}H_{25}NO_5$, is obtained; this is probably identical with Wackenroder's corydaline. It yields well characterised salts, including an aurochloride and platinochloride. From the chloroform solution (3), four bases were isolated, but were not investigated further.

A. J. G.

Geissospermine. By M. Freund and C. Fauvet (*Ber.*, **26**, 1084—1085).—Hesse (Abstr., 1880, 675) obtained from pereiro bark (*Geissospermum Vellosii*) a crystalline alkaloïd, geissospermine, and an amorphous alkaloïd, pereirine, melting at 124°.

The authors have examined a crystalline alkaloïd which has for some time been placed on the market by the firm of Trommsdorf under the name of geissospermine. Analyses of the base and of its salts show that it has the formula $C_{23}H_{28}N_2O_4$; its salts contain but one equivalent of acid, and in this respect as well as in its physiological action it resembles brucine. It melts at 189°, and is readily converted into an amorphous *base* $C_{46}H_{54}N_4O_7$, which is tetracidic, melts at 60—70°, yields a *methiodide* melting at 265°, and, when fused with potash, gives rise to a crystalline *base* melting at 151°.

A. R. L.

Stachydrine. By A. v. PLANTA and E. SCHULZE (*Ber.*, **26**, 939—942).—*Stachydrine* is the name adopted by the authors for the base resembling betaïne, from *Stachys tuberifera* (Abstr., 1890, 1183). They describe methods for its isolation. The *hydrochloride*, $C_7H_{13}NO_2.HCl$, crystallises in transparent prisms, is readily soluble in water, and differs from betaïne hydrochloride both in composition and in being soluble in cold absolute alcohol. The *platinochloride*, $(C_7H_{13}NO_2)_2,H_2PtCl_6$, forms large, orange-red, rhombic crystals containing $2H_2O$, $a:b:c = 0{\cdot}6082 : 1 : 0{\cdot}8277$; the *aurochloride* crystallises in small, yellow prisms. The free *base*, obtained by treating the hydrochloride with silver oxide, forms colourless, transparent crystals which deliquesce in the air, and become opaque with the loss of water of crystallisation at 100°; it melts at 210°, and its aqueous solution has not an alkaline reaction. A. R. L.

Amyloïd, a Component of Milk and Dairy Products. By F. J. HERZ (*Chem. Zeit.*, **16**, 1594—1595).—During the microscopic investigation of milk, cream, curds, butter-fat, and lean cheese, and even of pure caseïn, the author has found structures which, as regards shape and size, are not unlike starch granules, and which also give a bluish colour with iodine. They are, however, not gelatinised on boiling with water, and are also insoluble in hot alcohol and ether.

The author thinks that they consist of a modification of albumin, and may perhaps be obtained in a pure state by treating milk or colostrum with pepsin and hydrochloric acid. L. DE K.

Oxyhæmatin, reduced Hæmatin, and Hæmochromogen. By H. BERTIN-SANS and J. MOITESSIER (*Compt. rend.*, **116**, 401—403).—Oxyhæmatin, prepared by Cazeneuve's process and dissolved in a 1 per cent., or 0·1 per cent., solution of sodium hydroxide, shows a single absorption band between C and D, the middle being about λ 618. The addition of a reducing agent, such as potassium sulphide, sodium hydrosulphide, ferrous tartrate, &c., produces the true spectrum of reduced hæmatin, a single absorption band, the middle of which practically coincides with D. This spectrum is not affected by the presence of an excess of the reducing agent. Reduced hæmatin, showing precisely the same spectrum, is obtained when the hæmatin has been dissolved in an alcoholic solution of sodium hydroxide or an aqueous solution of sodium carbonate.

If the solution of reduced hæmatin obtained in this way is mixed with a slight excess of ammonia, or of various amines, such as ethyl amine, aniline, glycocine, or taurine, the absorption band of reduced hæmatin rapidly disappears, and the spectrum of hæmochromogen becomes visible.

Carbamide and other amides do not produce this result.

A very minute quantity of albumin, on the other hand, converts the spectrum of reduced hæmatin into that of hæmochromogen. 0·05 milligram of albumin is sufficient to produce this change in 2 c.c. of the solution of reduced hæmatin, and hence it constitutes a very delicate test for albumin.

Hæmochromogen solution, when treated with a current of air, is reconverted into oxyhæmatin. The position of the two bands of hæmochromogen varies with the nature of the nitrogen compound added to the hæmatin but the middle of the first band, which is the more intense and better defined, oscillates about λ 560.

It follows, from these results, that when oxyhæmatin in alkaline solution is treated with reducing agents in absence of ammonia and other nitrogen compounds, it yields *reduced hæmatin*, which has a characteristic spectrum, whilst in presence of ammonia, amines, albumin, &c., hæmochromogen is formed. The differences in the spectrum of hæmochromogen are not due to the differences in the composition of the solvent, and it would seem that several hæmochromogens exist.

C. H. B.

Action of Carbonic Oxide on Reduced Hæmatin and Hæmochromogen. By H. Bertin-Sans and J. Moitessier (*Compt rend.*, **116**. 591—592).—When carbonic oxide is passed into an alkaline solution of freshly prepared reduced hæmatin (preceding abstract), the single absorption band is replaced by two bands similar to those of carbonylhæmoglobin. The carbonic oxide, however, is very easily displaced by oxygen or air. Out of contact with air, the carbonic oxide is displaced by hydrogen, but the change takes place much more slowly.

If excess of ammonia is added to the solutions of carbonylhæmatin, the appearance of the spectrum changes immediately, and the two bands (which correspond approximately to λ 569 and λ 531) are replaced by two more distinct and intense bands at λ 590 and λ 546, the first being the narrower, more intense, and better defined of the two. The same phenomena are obtained by the direct action of carbonic oxide on the hæmochromogen obtained by the action of a reducing agent on ammoniacal solutions of oxyhæmatin (compare Popoff, *Centr. f. d Med. Wiss.*, 1868). The ammonia not only alters the spectrum, but also increases the stability of the compound, the carbonic oxide being displaced much more slowly by oxygen.

If an excess of albumin is added to the solution of carbonylhæmatin, the appearance of the spectrum does not alter, but the compound becomes much more stable in presence of air, and addition of ammonia has no effect on the spectrum. The spectrum has exactly the same appearance as that of the compound formed by the action of carbonic oxide on hæmochromogen that has been prepared in presence of albumin. The instability of carbonylhæmatin, especially in the absence of albumin, and the effect of ammonia on its spectrum, distinguishes it readily from carbonylhæmoglobin. C. H. B

Organic Chemistry.

Preparation of Tetriodoethylene. By L. Maquenne (*Bull. Soc. Chim.* [3], **7**, 777—778).—A simpler method of preparing tetriodoethylene, C_2I_4, than that described by Moissan (Abstr., 1892, 1291) consists in adding an excess of potash to an aqueous solution of acetylene, and subsequently dropping in iodine in small portions, when the tetriodoethylene separates as a crystalline precipitate. It is also obtained when crude barium carbide (Abstr., 1892, 685; this vol., i, 62) is treated with an equal weight (30 grams) of iodine dissolved in benzene (75—100 c.c.); water is now added drop by drop until effervescence ceases, when the benzene solution is decanted from the pasty mixture of magnesia (from the crude barium carbide), the latter extracted with boiling benzene, and the united benzene solutions distilled and finally evaporated to dryness; the tetriodoethylene is then washed with alcohol and crystallised from hot benzene. The pure compound (6 grams) melts at 192° (corr.). The compound of lower melting point obtained by Homolka and Stolz (Abstr., 1885, 1198) must have been impure. A. R. L.

Substitution in the Fatty Series. By A. D. Herzfelder (*Ber.*, **26**, 1257—1261).—Although propylenic bromide yields tribromhydrin when brominated, yet propylenic chloride does not yield trichlorhydrin, $CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl$, boiling at 154—156°, when treated either with antimony pentachloride (1 mol.), or with liquid chlorine and iron. The trichloropropane actually formed, which is also formed when propylic chloride is treated with antimony pentachloride (2 mols.), boils at 132°, and differs also from that obtained by the action of antimony chloride on acetone chloride, which boils at 121°, and has the constitution $CH_3{\cdot}CCl_2{\cdot}CH_2Cl$. It must, therefore, have the only remaining formula $CH_3{\cdot}CHCl{\cdot}CCl_2$, and the old boiling point—"about 140°"—formerly given for this substance is incorrect.

When propylic, isopropylic, butylic, isobutylic, and tertiary butylic chlorides, all containing either the group $>CCl{\cdot}CH_3$ or $>CH{\cdot}CH_2Cl$, are heated with bromine and iron wire, they all give dibromides containing the group $>CBr{\cdot}CH_2Br$. Isoamylic chloride, under similar circumstances, yields a monobromide, $CHMe_2{\cdot}CH_2{\cdot}CH_2Br$.

C. F. B.

Formation of Amylic Salts from Acids and Amylene. By W. Nernst and C. Hohmann (*Zeit. physikal. Chem.*, **11**, 352—390).—The formation of amylic salts from acids and amylene (trimethylethylene) has already been investigated by Menschutkin and Konovaloff (Abstr., 1888, 340 and 1167), the latter coming to the conclusion that the change is one which does not follow the ordinary law of mass action. This conclusion was, however, as shown by the authors, based upon an incorrect application of the above law, a recalculation of the numbers given by Konovaloff for the action of dichloracetic acid on amylene giving results in perfect accordance with those demanded

by theory. It therefore appeared desirable to submit the action of acids on amylene to a further examination, in order to ascertain whether the law of mass action holds throughout.

The acids taken were di- and tri-chloracetic, trichlorobutyric, trichlorolactic, salicylic, and benzoic. Amylic trichloracetate was prepared in the course of the experiments in a pure condition. It is a colourless liquid, of sp. gr. 20·4°/4° = 1·202, and specific refraction n 20·4°/D = 1·44758.

The formation of the ethereal salts takes place in all cases in accordance with the law of mass action. The limit to the action of an acid is defined by its affinity coefficient, this being carried further the greater the electrolytic dissociation in water of the acid in question. The action is also proportional to the square of the concentration of the acid. H. C.

Action of Mercury Salts on Unsaturated Hydrocarbons and Alcohols. By M. G. KUTCHEROFF (*J. Russ. Chem. Soc.*, **24**, 330—333).—With a solution of mercuric chloride, diallyl gives an abundant white precipitate, insoluble at the ordinary temperature in water or alcohol, but which dissolves easily in caustic alkalis, and may be reprecipitated from the solution by neutralisation. Acids, even acetic acid, dissolve it with liberation of diallyl. The empirical formula of the compound is $C_6H_{10},HgCl_2.HgO,H_2O$. A similar substance having the composition $2C_2H_4,HgCl_2,HgO$ is precipitated when ethylene acts on an aqueous solution of mercuric chloride. It is slightly soluble in water and in alcohol, easily soluble in alkalis, and regenerates ethylene when treated with acids. The author attributes the following constitutions to these compounds:—

$$C_2H_4(CH{:}CH{\cdot}HgCl)_2 + 2H_2O \text{ and } 2CH_2{:}CH{\cdot}HgCl + H_2O.$$

Allyl alcohol at the ordinary temperature gives a white, crystalline precipitate with aqueous mercuric chloride; this is soluble in alkalis, and has the composition $O(C_3H_4{\cdot}HgCl)_2$. It may be considered as the compound of allyl ether corresponding with the above-mentioned compounds of diallyl and ethylene, and can, in fact, be formed directly from the ether and mercuric chloride. Allyl alcohol when heated for several hours at 100° with mercuric chloride is converted for the most part into allyl ether without any trace of allylic chloride being formed. Calomel and the compound $O(C_3H_4{\cdot}HgCl)_2$ are the other products.

Negative results were obtained with commercial amylene.

J. W.

Synthesis of Erythritol. By G. GRINER (*Compt. rend.*, **116**, 723—725).—When erythrene, $CH_2{:}CH{\cdot}CH{:}CH_2$ is dissolved in a large quantity of chloroform, cooled at −21° and treated with bromine, it yields a liquid dibromide, $C_4H_6Br_2$, boiling at 74—76° under a pressure of 26 mm. This compound is unstable in the liquid form, but at 100° it is very rapidly converted into a solid of the same composition, melting at 53—54°, and boiling at 92—93° under a pressure of 15 mm. It is very volatile, sublimes easily, has a piquant odour, and is very irritating to the eyes.

When this dibromide is heated at 125—130° for eight hours with

a slight excess of silver acetate and some acetic anhydride, it yields a diacetin, $C_4H_6(OAc)_2$, boiling at 110° under a pressure of 20 mm., and this combines readily with bromine forming the compound $C_4H_6Br_2(OAc)_2$ melting at 87°. The latter, when treated with silver acetate, yields a tetracetin, $C_4H_6(OAc)_4$, identical with that obtained from erythritol, and this tetracetin, when heated with concentrated barium hydroxide solution at 100°, yields erythritol, identical with the natural product in composition, melting point, crystalline form, and absence of optical activity. C. H. B.

Trehalase, a Ferment for Trehalose. By E. Bourquelot (*Compt. rend.*, **116**, 826—828).—The author's previous researches have shown that trehalose is almost always present in fungi, but only appears when the production of spores commences, and is localised in the tissues, and more especially in the vegetative tissue of the fruit or sporophore; it disappears gradually during ripening. Glucose cannot be detected in fungi until trehalose has made its appearance, but persists after the latter has disappeared. These facts indicated the presence of some ferment capable of converting trehalose into glucose, and the author has isolated such a ferment in the following manner.

Aspergillus niger is cultivated on Raulin's fluid, and when the liquid is covered with abundant fructifications, the growth is removed, its lower surface washed with water, triturated with dry sand, and left in contact with alcohol of 95° for five or six hours, after which it is collected and dried in a vacuum. It is then treated with water, again filtered, and the filtrate reprecipitated with alcohol, the precipitate being washed with alcohol and dried in a vacuum.

If a fermenting liquid only is required, it is sufficient to draw off the liquid when the mould is in full fructification and replace it by distilled water.

The ferment thus obtained completely converts trehalose into glucose, 1 mol. of the former yielding 2 mols. of the latter. Trehalose from the *tréhala* and trehalose from fungi both behave in precisely the same way under the influence of the ferment. Invertin from yeast, the diastase of the saliva, and emulsin have no action on trehalose. The author proposes to call the special ferment *trehalase*.

The product obtained also acts on maltose. It would seem, therefore, either that one and the same ferment acts on both trehalose and maltose, or that the product is a mixture of two ferments. Attempts to isolate two substances by fractional precipitation gave negative results. The power to ferment trehalose, however, diminishes above 54°, and completely disappears at about 63°, whereas the power to ferment maltose remains undiminished at 64°, and only disappears between 74° and 75°. It follows that the product obtained in the manner described is really a mixture of two substances, the one fermenting maltose, and the other fermenting trehalose. C. H. B.

Calcium Sucrates. By P. Petit (*Compt. rend.*, **116**, 823—826).—The action of sodium hydroxide solution on a mixed solution of

. accharose and calcium chloride in a calorimeter gives the following results.

$Ca(OH)_2$ sol. + $C_{12}H_{22}O_{11}$ diss. = $CaO,C_{12}H_{22}O_{11}$ diss. ..... develops + 7·2 Cal.

$2Ca(OH)_2$ sol. + $C_{12}H_{22}O_{11}$ diss. = $2CaO,C_{12}H_{22}O_{11}$ diss. ..... „ +11·7 „

With a higher proportion of calcium oxide there is no further thermal disturbance, and hence it would seem that only two calcium sucrates exist at the ordinary temperature. The action of monocalcium sucrate on freshly precipitated calcium hydroxide leads to the same value, +4·5 Cal., for the formation of the dicalcium sucrate. The following table shows the quantity of calcium oxide dissolved by 1 gram-molecule of sugar in various proportions of water.

Water.....	20	10	8	6	5	4	litres.
CaO	56·07	56·10	56·14	59·2	63·15	70·24	grams.

Water.....	3	2	1·5	litres.
CaO	78·88	88·06	93·28	grams.

The curve representing these results indicates that at infinite concentrations 2 mols. of calcium oxide would be dissolved.

Monocalcium sucrate combines with saccharose, the heat developed by the addition of various proportions of saccharose to 1 mol. of the sucrate being as follows.

1 mol.	2 mols.	3 mols.	5 mols.	7 mols.
+1·68	+2·8	+3·1	+2·9	+3·1 Cal.

It appears that beyond 3 mols. the thermal disturbance becomes constant, and hence there is one compound, $CaO,C_{12}H_{22}O_{11},3C_{12}H_{22}O_{11}$, formed with development of +3·1 Cal.

The author was unable to obtain a tricalcium sucrate. When a sucrate solution containing 19·2 per cent. of calcium oxide is heated at 100°, a dicalcium sucrate is obtained, but it is only slightly soluble in water, and when treated with hydrochloric acid, the heat of formation obtained is +5·4 Cal. It follows that heat modifies the sucrates very considerably, probably because calcium oxide acts on saccharose in much the same way as on maltose. C. H. B.

Action of Metaphosphoric acid on Organic Bases. By W. Schlömann (*Ber.*, **26**, 1020—1025).—The following bases in ethereal solution form amorphous metaphosphates on the addition of metaphosphoric acid (prepared by dissolving phosphoric anhydride in 4 parts of water): Methylamine, ethylamine, propylamine, amylamine, allylamine, ortho- and para-toluidine, xylidine, α- and β-naphthylamine, benzylamine, anisidine, phenylhydrazine, unsymmetrical diphenylhydrazine, α-benzylphenylhydrazine, ethylenediamine, pentamethylenediamine, benzidine, ortho- and para-phenylenediamine, and toluylenediamine. These salts are generally soluble in water or in excess of the acid, but insoluble in alcohol.

The metaphosphates of the following bases are readily soluble in ether, β-benzylphenylhydrazine, piperidine, methylaniline, diphenylamine, diamylamine, hydrazobenzene, pyridine, quinoline, and dimethylaniline.

Solutions containing 3 per cent. of aniline and 0·1 per cent. of phenylhydrazine give precipitates with solutions of metaphosphoric acid containing 12·5 per cent. of phosphoric anhydride. On treating a mixture of aniline and methylaniline with metaphosphoric acid solution, the aniline is completely precipitated, but carries down some of the methylaniline salt.

β-Benzylphenylhydrazine, $NHPh{\cdot}NHC_7H_7$, is prepared by heating phenylhydrazine with 2 molecular proportions of benzylic chloride for 24 hours at 160°; it crystallises in pale yellow needles melting at 155·5°. J. B. T.

Action of Nitrous acid on Tetramethylenediamine. By N. Demyanoff (*J. Russ. Chem. Soc.*, **24**, 346—355).—Tetramethylenediamine was prepared by reducing ethylenic dicyanide by means of sodium in methyl alcohol solution, and from its hydrochloride the nitrite was obtained by grinding it up with water and silver nitrite at the ordinary temperature. On heating an aqueous solution containing 50 grams of tetramethylenediamine nitrite in 1 litre of water, decomposition took place at 80—90°, and the heating was continued until a temperature of 130° was reached. Nitrogen was given off along with a gas which did not condense in the receiver, but was absorbed by bromine. The aqueous distillate was quite homogeneous, neutral, slightly yellow, and of an offensive odour.

The bromide formed by the union of the gaseous product of decomposition with bromine was a crystalline solid melting at 115—116°. Investigation showed it to be the tetrabromide of erythrene, $CH_2{:}CH{\cdot}CH{:}CH_2$, which is consequently the hydrocarbon formed in the decomposition.

In the aqueous distillate, there were detected nitrosopyrrolidine, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!N{\cdot}NO$, tetrahydrofurfuran, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!O$, boiling at 67°, and an unsaturated alcohol of the formula $C_4H_7{\cdot}OH$. The latter boiled at 112—114°, and had a sp. gr. of 0·8635 at 0°/0°, and 0·8484 at 18·5°/0°. When heated with fuming hydrobromic acid, it gave a saturated dibromhydrocarbon, $C_4H_8Br_2$, boiling at 174—175°, and having a sp. gr. of 1·829 at 0°/0°. The dibromhydrocarbon,

$$CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2Br,$$

obtained from aldol by reduction and heating with fuming hydrobromic acid, was proved to be identical with the bromide from the unsaturated alcohol, which, therefore, must have the constitution $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ or $CH_2{:}CH{\cdot}CHMe{\cdot}OH$. The rate of etherification points to the first formula as being correct.

The brown residue which did not distil over at 130° consisted of two glycols, tetramethylene glycol, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and the glycol $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. J. W.

Action of Ammonia and of Aliphatic Amines on Acetylacetone. By A. COMBES and C. COMBES (*Bull. Soc. Chim.* [3], **7**, 778—788).—*Acetylacetonamine*, $CHAc{:}CMe{\cdot}NH_2$, is formed with the elimination of water when the additive compound of ammonia and acetylacetone (*Bull. Soc. Chim.* [2], **49**, 577) is gently heated in a current of ammonia and the product distilled; the compound passes over at 209°, solidifies in crystals on cooling, and melts at 43°. It undergoes hydrolysis when its aqueous solution is heated, and acids exert the same effect in the cold. The *hydrochloride* formed by passing dry hydrogen chloride into an ethereal solution of the compound dissociates on exposure; the copper derivative, $(C_5H_8NO)_2Cu$, is crystalline. It reacts with methylic iodide, forming methylacetylacetone, and when it is heated at 220° for 15—18 hours, it blackens, and several basic compounds are formed, one of which has the formula $C_{15}H_{18}N_2$, and melts at 85°.

Acetylacetone reacts with ethylamine, forming a *compound*, $CHAc{:}CMe{\cdot}NHEt$, which boils at 210—215°, and with diethylamine, forming a *compound*, $CHAc{:}CMe{\cdot}NEt_2$, boiling at 155—156° (24 mm.), but it does not act on tertiary amines. With ammonia, methylacetylacetone yields a *compound*, $CMeAc{:}CMe{\cdot}NH_2$, melting at 105°.

Dimethylacetylacetone, $CMe_2Ac{\cdot}COMe$, prepared by the action of methylic iodide on the sodium derivative of methylacetylacetone, boils at 175—177°. It does not react with ammonia, a fact which indicates that acetylacetone and the other compounds react with ammonia in a tautomeric form, $RCO{\cdot}CH{:}C(OH)R$, in which they contain a mobile (hydroxylic) hydrogen atom; it also justifies the adoption of the above formulæ for the amido-compounds.

Secondary amines containing an aromatic radicle do not react with acetylacetone. A. R. L.

Action of Diamines on Acetylacetone. By A. COMBES and C. COMBES (*Bull. Soc. Chim.* [3], **7**, 788—793).—The compound formed by the action of ethylenediamine on acetylacetone has already been described (Abstr., 1889, 851). The compound $C_7H_{12}N_4O_2$, obtained by the action of carbamide on acetylacetone (Evans, this vol., i, 129) melts at 200° with decomposition. Acetylacetone reacts with guanidine carbonate, forming an *amidodimethylpyrimidine*,

$$CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{:}N\\CMe{\cdot}N\end{matrix}\begin{matrix}>\\<\end{matrix}C{\cdot}NH_2.$$

It separates from hot concentrated aqueous solutions in an anhydrous condition, and melts at 153°, but, on allowing a saturated solution to slowly cool, crystals containing $2\frac{1}{2}H_2O$ are obtained.

A. R. L.

Tar from the Bark of Populus tremula. By N. FARMAKOVSKY (*J. Russ. Chem. Soc.*, **24**, 423—439).—The tar obtained from the dry distillation of *Populus tremula* is strongly acid, 1000 grams requiring 30 grams of anhydrous potassium carbonate for its neutralisation. The acid constituents are the lower fatty acids up to valeric acid, phenols (about 17 per cent.), and benzoic acid (about $\frac{1}{2}$ per cent.).

Hydrocarbons form the remainder of the tar. Its sp. gr. at 17°/17° is 0·956. J. W.

Condensation of Aliphatic Aldehydes with Cyanacetic acid. By E. Fiquet (*Bull. Soc. Chim.* [3], **7**, 767—771).—The condensation of aliphatic aldehydes with cyanacetic acid is quite analogous to that of aromatic aldehydes (Abstr., 1892, 1340). *Cyanocrotonic acid*, $CHMe{:}C(CN)\cdot COOH$, is obtained by heating cyanacetic acid with an excess of acetaldehyde at about 93—95°. Care must be taken, as the acid decomposes at about 95°, and other condensations take place when the heating is protracted. The new acid crystallises in delicate, colourless needles, melts at 92°, is very soluble in water, and forms crystalline alkali salts. It yields malonic acid and ammonia when heated with potash, and oxalic acid when heated with nitric acid; when distilled, crotononitrile passes over at 120°. Trichlorocyanocrotonic acid is formed by heating a mixture of cyanacetic acid, chloral, and glacial acetic acid in a reflux apparatus for 48 hours.

Hexylcyanacrylic acid, $CH_2Me\cdot[CH_2]_4\cdot CH{:}C(CN)\cdot COOH$, is prepared by boiling together a mixture of œnanthaldehyde, cyanacetic acid, and glacial acetic acid for 60 hours; it crystallises in nacreous laminæ, and melts at 116—118°.

Cyanacetic acid and glyoxylic acid react at 180°, forming a crystalline product melting at 210°; it may be either *cyanofumaric* or *cyanomalonic acid*. A. R. L.

Brom-additive Products of Angelic and Tiglic acids. By J. Wislicenus (*Annalen*, **274**, 99—119).—A rejoinder to Fittig (this vol., i, 188). The author brings forward fresh experimental evidence in support of his views (*ibid.*, i, 135). A. R. L.

Turkey-red Oil. By P. Juillard (*Chem. Centr.*, 1893, i, 185—187; from *Bull. Soc. indust. Mulhouse*, 1892, 415—491).—The products of the action of sulphuric acid on castor and olive oil, which are employed as substitutes for the original Turkey-red oil, have been the subject of numerous investigations; see Frémy (*Annalen*, **65**, 121), Liechti and Suida (Abstr., 1884, 238), Benedict and Ulzer (Abstr., 1887, 914), and others.

The author finds that the initial product of the action of sulphuric acid on ricinoleïc acid is ricinosulphuric acid, which reacts with another molecule of ricinoleïc acid to form diricinosulphuric acid, which then hydrolyses in part into diricinic acid. Sulphuric acid can react with the latter, so that the red oil obtained in this manner consists of a mixture of mono- and poly-ricinic acids, and of mono- and poly-ricinosulphuric acids. With sulphuric acid, castor oil gives first ricinoleïnsulphuric acid and a diricinoleïnsulphuric acid, $OH\cdot C_{17}H_{32}\cdot COO\cdot C_3H_5(OH)O\cdot CO\cdot C_{17}H_{32}O\cdot SO_2\cdot OH$, which is soluble in water. Polyricinic acids and polyricinosulphuric acids are also formed. Diricinosulphuric acid decomposes on hydrolysis with boiling alcoholic potash, in a manner typical of the polyricinosulphuric acids, into ricinic acid and ricinosulphuric acid, but with dilute acids into sulphuric acid and diricinic acid. Diricinoleïnsulphuric acid is converted by

alkali hydroxides and carbonates into ricinosulphuric acid, ricinic acid, and glycerol; whilst, when heated at 90° with a little dilute hydrochloric acid, sulphuric acid, glycerol, and polyricinosulphuric acid are the products. It is usual to wash the crude product with a concentrated solution of sodium sulphate to free it from acid; the author shows that the ricino- and ricinoleïn-sulphuric acids are thereby converted into their acid or normal salts according as they contain a single carboxyl group or otherwise.

For the estimation of the molecular weights of these acids by the cryoscopic method, the author employs phenol as solvent, taking the molecular depression of this compound to be 67·5. Eykman's value (76) is only correct with phenol for the ethereal salts of some bibasic acids. *Ricinic acid* is a syrup; the semi-fluid mass obtained by the decomposition of ricinosulphuric acid contains a compound of dehydrostearic acid with ricinic acid of melting point 70—73°. *Ethylic ricinate* is an oil which is not hydrolysed by 5 per cent. soda, but when shaken with hydrochloric acid of 20° B., it is converted into polyricinic acids. Acetyl and butyryl derivatives were also prepared.

Oleoricinic acid, $C_{17}H_{33}\cdot COO\cdot C_{17}H_{32}\cdot COOH$, is obtained by allowing a mixture of oleïc acid (20 grams), ethylic ricinate (10 grams), and hydrochloric acid of 20° B. (50 grams) to remain for a month. Polyricinic acids are formed:—1, By the action of hydrochloric acid on Turkey-red oils; 2, by the spontaneous decomposition of the acid red oil; 3, by heating ricinic acid with a little ricinosulphuric acid at 105—110°; 4, by the action of hydrochloric acid on ricinic acid and castor oil. Their purity is controlled by means of the cryoscopic method. The remainder of the paper seems to be purely technical. The preparation of red oil from ricinic acid, from castor oil, from oleïc acid, and from oleïn is described. A. R. L.

Condensation of Alkylic Acetocyanacetates with Phenol. By A. Held (*Compt. rend.*, **116**, 720—723).—A mixture of ethylic acetocyanacetate and phenol in molecular proportion is added in successive small quantities to an excess of well-cooled concentrated sulphuric acid, allowed to remain in contact at the ordinary temperature for at least 24 hours, and then poured into cold water or over crushed ice. The product crystallises from ether in large, colourless, prismatic crystals melting at 110°; it is insoluble in water, but dissolves in alcohol, ether, and glacial acetic acid. The alcoholic solution gives an intense red coloration with ferric chloride. The compound has the composition $CON_2H_2\cdot CHAc\cdot COOEt$, and is produced by simple hydration of the ethylic acetocyanacetate. When boiled with the calculated quantity of potassium hydroxide until evolution of ammonia ceases, it yields alcohol and acetic and malonic acids.

In the absence of phenol, sulphuric acid diluted with even a small quantity of water has no action on ethylic acetocyanacetate, but with the concentrated acid, after several weeks' contact, hydration does take place, although to a considerably smaller extent than when phenol is present.

With resorcinol in place of phenol, the results under the same conditions are quite different, and the product is the β-methylumbelliferone

obtained by Pechmann and Duisberg by the action of resorcinol on ethylic acetoacetate in presence of sulphuric acid. In the process of hydration, the nitrogen is eliminated in the form of ammonia.

Methylic acetocyanacetate remains unaltered after contact with concentrated sulphuric acid for several weeks at the ordinary temperature, either in presence or absence of phenol. At a higher temperature, it splits up into acetic and carbonic acids, ammonia, and alcohol.

Methylic acetocyanacetate and resorcinol, in presence of sulphuric acid, yield no appreciable quantity of methylumbelliferone, although the fact that the mother liquors, after supersaturation with alkali, show a greenish-blue fluorescence, indicates that some slight change has taken place.

Dehydrating agents other than sulphuric acid, such as zinc chloride or aluminium chloride, gave negative results. C. H. B.

Oxalic acid Derivatives. By A. Rosenheim (*Ber.*, **26**, 1191—1194).—Tungstic anhydride is dissolved when boiled with potassium oxalate solution; after separation from tungstic acid and evaporation, colourless, crystalline plates are deposited; these have the formula $K_2C_2O_4,WO_3 + H_2O$, and are decomposed by hydrochloric acid immediately, and by sulphuric acid more slowly. The corresponding *sodium* and *ammonium* salts resemble the potassium salt, but are more readily soluble.

By the action of molybdic anhydride on ammonium oxalate, two salts are obtained; the more readily soluble, $C_2O_4(NH_4)_2,MoO_3 + H_2O$, can be purified by recrystallisation, when it forms lustrous needles. The second salt, $C_2O_4(NH_4)_2,2MoO_3$, crystallises in white crusts, and undergoes decomposition on treatment with hot water. A third salt is prepared by the action of hydrogen ammonium oxalate on molybdic anhydride; it crystallises in prisms, and has the formula

$$(NH_4)_2O,2C_2O_3,2MoO_3,3H_2O.$$

The preceding compounds may also be obtained from hydrogen ammonium oxalate and hydrogen ammonium molybdate. The corresponding *potassium* and *ammonium sodium salts* are crystalline; the *sodium salts* do not crystallise.

A double *ammonium vanadium oxalate*, $3(NH_4)_2O,4C_2O_3,V_2O_5,4H_2O$, crystallising in long, yellow prisms, is prepared from ammonium oxalate and vanadic anhydride, or from hydrogen ammonium oxalate and ammonium metavanadate. The corresponding *sodium* and *potassium* salts have also been obtained. J. B. T.

Stereochemistry of Malic Derivatives: Variations in the Rotatory Power of Liquids. By A. Colson (*Compt. rend.*, **116**, 818—820).—Acetylmalic acid, obtained by the action of the anhydride on water, melts at 139°, and is very soluble in warm water, 1 part of water dissolving 2 parts of the acid at 50°. Its specific rotatory power lies between $-10°$ and $-11°$, whatever the degree of concentration of the solution. The author considers that the sign of the

rotatory power is contrary to that which would have been predicted by stereochemical theories.

Acetylmalates are usually soluble in water, but the ferric and silver salts are insoluble. Both the potassium and barium salts are lævogyrate, and the deviation seems to be independent of the base.

Acetylmalic anhydride, obtained by the action of acetic chloride on malic acid, is a white, nacreous substance which melts at 59°. At 60° a layer, 5 mm. in thickness, has a lævorotatory power of $-1°\ 40'$, whilst in superfusion at 25° the deviation falls to $-1°\ 15'$. Contrary to what happens in the case of acetyltartaric anhydride, acetylmalic anhydride has a rotatory power of the same sign as the corresponding acid.

In reply to Aignan (this vol., ii, 354), the author points out that his observations were made with the same compounds as those of Guye.

C. H. B.

Trichloromethanesulphonic Chloride. By T. Selivanoff (*J. Russ. Chem. Soc.*, **24**, 333—334).—The substance $CCl_3\cdot SO_2Cl$ is always obtained from carbon bisulphide, and cannot be prepared from trichloromethanesulphonic acid, of which it is supposed to be the acid chloride. The author contends that it is a mixed anhydride of trichloromethanesulphinic acid and hypochlorous acid, adducing the following evidence in support of his contention. The chloride can easily be reduced to the acid $CCl_3\cdot SO_2H$, and is converted by ammonia into the ammonium salt of this acid, $CCl_3\cdot SO_2NH_4$, nitrogen being liberated. The sulphinic acid and hypochlorous acid when mixed do actually give the compound $CCl_3\cdot SO_2Cl$. Ethylamine acts on it with formation of the compounds $NEtCl_2$ and NEt_2Cl, corresponding with the author's assumption of the presence of hypochlorous acid. Finally, 1 mol. of the chloride $CCl_3\cdot SO_2Cl$ liberates 1 mol. of iodine from a solution of potassium iodide. When boiled for a long time with an aqueous solution of caustic alkali, the chloride does give the alkali salt of trichloromethanesulphonic acid, but this the author attributes to the oxidising action of the alkali hypochlorite simultaneously present in the solution with the salt of the sulphinic acid primarily formed.

J. W.

Hydrolysis of Sulphones, Sulphonesulphinic Acids, and Sulphinolactones. By E. Baumann and G. Walter (*Ber.*, **26**, 1124—1139).—Both trimethylenedisulphone, $\begin{matrix}CH_2\cdot SO_2\\ CH_2\cdot SO_2\end{matrix}\!\!>\!CH_2$, and diethylenedisulphone, $\begin{matrix}CH_2\cdot SO_2\cdot CH_2\\ CH_2\cdot SO_2\cdot CH_2\end{matrix}$, in accordance with Stuffer's rule that sulphones containing sulpho-groups joined to adjacent carbon atoms are capable of being hydrolysed, yield, with baryta-water, hydroxyethylsulphonemethylenesulphinic acid,

$$OH\cdot CH_2\cdot CH_2\cdot SO_2\cdot CH_2\cdot SO_2H,$$

and hydroxyethylenesulphonethylenesulphinic acid,

$$OH\cdot CH_2\cdot CH_2\cdot SO_2\cdot CH_2\cdot CH_2\cdot SO_2H,$$

respectively; of these the latter, in accordance with the rule quoted,

can be further hydrolysed; not so the former, which contains two sulpho-groups united to the *same* carbon atom (compare Abstr., 1890, 987). Both these acids yield sulphinolactones which readily oxidise to sulphonolactones, and, in the second case, can be reconverted into the original disulphone.

Trimethylenedisulphone is obtained by condensing formaldehyde with ethylene mercaptan in the presence of alcoholic hydrochloric acid, and oxidising the ethylenemercaptal so formed with permanganate and dilute sulphuric acid. It forms rhombic tables melting at 204—205°, and yields a *dichloro-* and a *dibromo-derivative* (melting with decomposition at 222—223° and 271° respectively), the two hydrogen atoms of the methylene group in $SO_2{\cdot}CH_2{\cdot}SO_2$ being replaced. By warming the sulphone with baryta-water, *hydroxyethylsulphonemethylenesulphinic acid* is formed as the *barium salt*; the *potassium salt* was also prepared. The acid itself is a syrup which when heated in aqueous solution loses sulphurous anhydride and yields *hydroxyethylmethylsulphone*, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Me$, as a colourless, crystalline mass which melts at 20·5°, and is oxidised by chromic acid to *methylsulphoneacetic acid*, $COOH{\cdot}CH_2{\cdot}SO_2Me$; this, when heated, yields methylsulphone. A concentrated solution of the sulphinic acid, when allowed to evaporate spontaneously, gradually deposits quadrangular prisms of the *sulphinolactone*; this melts at 164°, and is oxidised by acid permanganate in the cold to the corresponding *sulphonolactone*, which forms hexagonal prisms, turns brown at 170°, and melts at 206—207°.

Diethylenedisulphone, obtained by oxidising diethylene bisulphide with acid permanganate, is converted by heating with baryta-water into *hydroxyethylsulphonethylenesulphinic acid*. On boiling the *barium salt* with water, it is partially reconverted into diethylenedisulphone; the *copper salt* was also prepared. The acid itself, in concentrated aqueous solution, forms a syrup which solidifies slowly, more quickly when warmed, to a crystalline mass of the *lactone*; this crystallises in needles which turn yellow at 190—200°, and melt with decomposition at 220—222. This lactone, when boiled with a few drops of aqueous sodium carbonate, is only partially reconverted into the sulphinic acid; the rest of it yields diethylenedisulphone. When oxidised with acid permanganate, it yields the corresponding *sulpholactone*, as needles or hexagonal plates which become discoloured at 220°, melt with decomposition at 255—256°, and with baryta-water yield the *barium salt* of the corresponding *sulphonic acid*. The *potassium* and *silver salts* of this acid were also prepared; the acid itself is a syrup which cannot be reconverted into its lactone. When hydroxyethylsulphonethylenesulphinic acid is boiled for several days with baryta-water, it is hydrolysed, forming, for the most part, glycol and ethylenedisulphinic acid, $SO_2H{\cdot}CH_2CH_2{\cdot}SO_2H$, but also, to a slight extent, the other possible product, hydroxyethylsulphinic acid, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2H$. The latter could not be isolated, but a substance, *diethylene oxide sulphone*, $O<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>SO_2$, was obtained, and this probably resulted from condensation of hydroxyethylsulphinic acid with glycol; it forms colourless plates, melts at 130°,

and volatilises unchanged. *Ethylenesulphinic acid* was obtained in the form of its *barium* and *silver salts;* the former, when oxidised with bromine water, yields the *barium salt* of the corresponding *disulphonic acid* as colourless prisms; when it is converted into the sodium salt, and the latter heated at 100° with ethylic iodide in dilute alcohol, *ethylenediethylsulphone*, $SO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Et$, melting at 136°, is obtained. C. F. B.

Hydrogenisation of Benzene. By N. Kijner (*J. Russ. Chem. Soc.*, **24**, 450—454).—Benzene (1 c.c.) was heated for 24 hours at 260—270° with hydriodic acid (25 c.c.) of sp. gr. 1·97. Some of the benzene remained unchanged, but the bulk was converted into hexahydrobenzene, no intermediate substances being formed. The further reduction to hexane is incomparably more difficult, for even after heating hexahydrobenzene for 35 hours with the same acid at 275—298°, only about a fifth part is converted into the saturated hydrocarbon. J. W.

Formation of Nitro-derivatives at Low Temperatures. By R. Pictet (*Compt. rend.*, **116**, 815—817).—At very low temperatures, the action of the ordinary nitrating mixture of sulphuric and nitric acids is materially modified. If a mixture of concentrated nitric and sulphuric acids is cooled to −55—65°, and mixed with successive small quantities of finely powdered naphthalene, also cooled to −65°, and the vessel is placed in a receptacle cooled to −110—120°, no action takes place below −60°, but if the sparks from a powerful Ruhmkorff coil are allowed to impinge on the liquid, reaction begins. At −50—55° the action begins without the aid of the spark, and hence −60° seems to be the limiting temperature of this reaction. Under these conditions the proportion of β-dinitronaphthalene formed is much higher than at the ordinary temperature. An average result is β-dinitronaphthalene, 46 per cent., α-nitronaphthalene, 22·7 per cent., and α-dinitronaphthalene, 31·3 per cent.

The use of low temperatures makes it possible to determine and utilise the direction of the maximum tendency of the chemical affinities of the constituents.

At −55° the weight of paranitrotoluene obtained by the direct nitration of toluene is 5·5 times as great as at 0°, and it follows that the para-group corresponds with the primary affinities of the constituents.

The limiting temperature for the nitration of phenol without the aid of the spark is −65°. By allowing the spark from a coil to play on the mixture, complete reaction can be produced without any apparent rise of temperature if the receptacle in which the vessel is placed is kept at from −110—120°. At −65° the weight of paranitrophenol obtained is five times as great as at −40°.

When converting dinitrobenzene into metanitraniline by the action of hydrogen sulphide in presence of ammonia, and then diazotising the metanitraniline, about double the yield is obtained by conducting all the operations at low temperatures. C. H. B.

Constitution of the Dihydroxythiobenzenes. By G. Tassinari (*Gazzetta*, **23**, i, 191—196; compare Abstr., 1892, 1316).—On nitrating diphenylsulphone and reducing the product, diamidodiphenylsulphone is formed; this is diazotised and treated with mercuric chloride. On boiling the double salt thus obtained with water, it yields a dihydroxydiphenylsulphone, which forms colourless needles melting at 190—191°, and is necessarily a meta-derivative. The author finds it to be identical with the sulphone obtained by oxidising the dihydroxythiobenzene melting at 130° (*Real. Accad. Linc.*, **4**, 47); the latter is hence a meta-derivative, and in the reaction between chloride of sulphur and parabromophenol, the sulphur enters the molecule in the ortho-position to the bromine. The author was unable to prepare orthodihydroxythiobenzene by reducing dibromodinitrothiobenzene with hydriodic acid or tin and hydrochloric acid (compare Purgotti, this vol., i, 330). W. J. P.

Bülow's Reaction and the Oxidation of Hydrazones. By H. v. Pechmann (*Ber.*, **26**, 1045—1047).—By the action of amylic nitrite on benzaldehydephenylhydrazone in ethereal solution, a tetrazone, $CHPh:N\cdot NPh\cdot NPh\cdot N:CHPh$, is formed; this crystallises from benzene in yellow needles, melts at 190°, and gives an intense blue colour with concentrated sulphuric acid. By the action of phenylhydrazine on the tetrazone, benzaldehydephenylhydrazone is regenerated. The compound is also formed by the mutual action of nitrosophenylhydrazone and benzaldehyde, and has already been obtained by Minunni (this vol., i, 97) by the oxidation of benzaldehydephenylhydrazone with mercuric oxide; he erroneously states the melting point to be 179—180°. The formation of the above tetrazone is analogous to that of osotetrazones from osazones; Bülow's test for hydrazones depends on the formation of a tetrazone and its subsequent reaction with sulphuric acid.

The author points out the advantages of amylic nitrite as an oxidising agent, particularly where the presence of moisture is undesirable. J. B. T.

Wessel's Dicarbo-base from Phenylhydrazine and Carbodiphenylimide and its Cyclic Decomposition Products. By C. Schall (*Ber.*, **26**, 1180—1191).—Wessel's dicarbo-base (Abstr., 1888, 1083) is readily prepared by fusing diphenylguanidine (2 mols.) with phenylhydrazine (1 mol.) for five minutes, ammonia being evolved; it is probably represented by the formula

$$NHPh\cdot N[C(NPh)\cdot NHPh]_2;$$

and should accordingly be termed *α-bis-diphenylformamidylphenylhydrazine*, the complex $C(NPh)\cdot NHPh$ being designated *diphenylformamidyl* (compare Markwald and Wolff, this vol., i, 25); the base, if prepared from technical materials, is purified by treatment with concentrated hydrochloric acid at 150°, and melts at 204°, instead of 200°, as stated by Wessel; on heating with hydrochloric acid at 200°, it is completely decomposed, aniline being formed; it reacts with phenylthiocarbimide, but the product is difficult to purify.

The *acetyl derivative*, $NPhAc{\cdot}N[C(NPh)NHPh]_2$, is prepared by the action of acetic anhydride on the base at 130°, and crystallises in slender, silky, lustrous needles melting at 174°. By the action of acetic anhydride at 200° on the acetyl derivative, or by treatment with benzoic anhydride and soda, a compound is obtained, together with acetanilide or benzanilide, which crystallises from alcohol in colourless, transparent, hexagonal laminæ, melts at 170°, and may be distilled under reduced pressure without decomposition. This substance is represented by one or other of the formulæ $NPhAc{\cdot}N<\begin{matrix}C{\cdot}NPh\\ \|\\ C{\cdot}NPh\end{matrix}>O$, $NPhAc{\cdot}N<\begin{matrix}C(NPh)\\ \|\\ C(NPh)\end{matrix}>O$; the former is the more probable, as the reduction product does not show strongly marked basic properties (see below). A molecular weight determination by Raoult's method confirms the above formula. The compound does not react with phenylthiocarbimide, carbon bisulphide, or alkalis. The *tribromo-derivative*, $C_{20}H_{12}N_4OAcBr_3$, crystallises in slender needles, and melts at 224—225°.

By the action of nitric acid on the compound $C_{22}H_{18}N_4O_2$ (m. p. 170°), the acetyl group is eliminated, and a nitro-derivative, $C_{20}H_{15}N_4O{\cdot}NO_2$, is obtained, which crystallises in colourless, slender needles, melts at 197·5°, volatilises without decomposition at 272°, and becomes pale red on exposure to air.

On heating the compound (m. p. 170°) with hydrochloric acid at 150—180°, the acetyl group is also eliminated, and a substance is formed which crystallises in long, silky, lustrous needles, melts at 161°, is unaltered at 300°, and gives a blue coloration with acetic chloride; the reaction probably proceeds in two stages, the compound $NHPh{\cdot}N<\begin{matrix}C{\cdot}NPh\\ \|\\ C{\cdot}NPh\end{matrix}>O$ being first formed, and then changing spontaneously into the isomeride $\begin{matrix}PhN{\cdot}CH{\cdot}NPh\\ |\quad\quad|\\ N{:}C\text{—}NPh\end{matrix}>O$. The substance does not react with hydroxylamine hydrochloride, phenylhydrazine, or phenylthiocarbimide at 150°; by the action of hydriodic acid and phosphorus at 150°, or of hydrochloric acid at 275°, aniline is formed. Benzoic anhydride appears to yield an *additive compound*, which crystallises in thick, colourless plates, and is decomposed by recrystallisation from acetic anhydride at 220—230°, the acetyl derivative being probably regenerated. The *picrate*, $C_{20}H_{18}N_4O,(C_6H_3N_3O_7)_2$, is unstable and crystalline. The *dibromo-derivative* is formed by the action of bromine at ordinary temperatures, and melts at 178°; the *tribromo-compound* is obtained on heating with bromine in acetic acid solution; it crystallises in needles, melts at 227°, and decomposes at 300°. Two nitro-compounds have been prepared; the trinitro-derivative, $C_{20}H_{13}N_4O(NO_2)_3$, is formed at ordinary, the *dinitro-derivative*, $C_{20}H_{14}N_4O(NO_2)_2$, at higher, temperatures; the first crystallises from nitrobenzene in orange needles, softens at 291—295°, and melts at 363°; the second is deposited from acetic acid in red plates, and from nitrobenzene in nodular aggregates, which melt at 253°.

On reducing the acetyl compound, $C_{20}H_{15}N_4OAc$ (m. p. 170°), with sodium in amyl alcoholic solution, a neutral substance, which

melts at 218—219°, is obtained, together with ammonia, aniline, and in small quantity an oily base.

β-Benzoyl-α-bis-diphenylformamidylphenylhydrazine,

$$NPhBz{\cdot}N[C(NPh){\cdot}NHPh]_2,$$

is prepared from benzoic anhydride and the dicarbo-base, and crystallises in slender needles melting at 149°. On treatment with soda, benzanilide is eliminated, and a compound, $C_{20}H_{15}N_4OBz$, is formed, which is deposited in hexagonal needles melting at 172°. It does not combine with picric acid; by the action of hydrochloric acid, the benzoyl group is eliminated, and the compound (m. p. 161°) described above is formed. The *bromo-derivative*, $C_{20}H_{14}BrN_4OBz$, melts at 154°. The *dinitro-derivative*, $C_{20}H_{13}N_4O(NO_2)_2Bz$, crystallises with 1 mol. of acetic acid, melts at 130°, decomposes at 131—136°, resolidifies at 140°, and finally melts at 200°.

The author explains the action of benzoic or acetic anhydride on bis-diphenylformamidylphenylhydrazine by assuming that an additive compound, $NHPh{\cdot}N<\begin{matrix}C(NHPh){\cdot}NPh{\cdot}OR\\ C(NHPh){\cdot}NPh{\cdot}R\end{matrix}$, is first formed (R = Ac or Bz); substitution then takes place, and the additive compound is decomposed by alcohol; in presence of soda, the action proceeds further, and the group NHPhR is eliminated.

Bis-diphenylformamidylphenylhydrazine yields a *dimethyl derivative*, $NPh{:}C(NHPh){\cdot}N(NMePh){\cdot}CMe{:}NPh$, which forms an unstable, yellow powder melting at 227—232°, with decomposition; the *hydrochloride* is also unstable; the *hydriodide* occurs in two modifications melting at 258—260°; the one crystallises from alcohol in yellow needles, the other forms white plates, and is converted into the yellow compound by fusion, or by solution in glacial acetic acid; it does not dissolve in any other medium. J. B. T.

Hippurylphenylbuzylene; New Synthesis of Azoimide. By T. Curtius (*Ber.*, **26**, 1263—1271).—It is reasonable to suppose that when diazobenzene reacts with hydrazine, the two substances first unite to form a compound, $NPh{:}N{\cdot}NH{\cdot}NH_2$, and this then breaks up in two ways, yielding in one case diazobenzenimide and ammonia, in the other, aniline and azoimide. As a matter of fact, this does take place, but the intermediate compound cannot be isolated; the four decomposition products were, however, obtained, the last two in amount corresponding with only 10 per cent. of the theoretical.

An intermediate product is, however, obtained when cooled aqueous solutions of diazobenzene sulphate and hippurylhydrazine are mixed, and separates out in almost colourless, crystalline plates. It has the constitution $NPh{:}N{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NHBz$, and is named *hippurylphenylbuzylene*. It melts at 86°, and is instantaneously decomposed by aqueous alkalis or alkali carbonates, or by dilute acids, yielding chiefly diazobenzenimide and hippuramide, but also aniline and the decomposition products of diazohippuramide, namely, azoimide and hippuric acid.

From diazobenzene sulphate and benzoylhydrazine, *benzoylphenylbuzylene*, $NHBz{\cdot}NH{\cdot}N{:}NPh$, is obtained in a similar manner as a

colourless, crystalline precipitate; it decomposes partially while it is being filtered and dried, yielding diazobenzenimide and benzamide, with some aniline and benzoylazoimide. C. F. B.

Basic Bye-product obtained on benzylating Acetoxime. By E. Beckmann and A. Köster (*Annalen*, **274**, 37—41).—Beckmann, when benzylating acetoxime (*Ber.*, **22**, 439), obtained a bye-product melting at 122—123°. The authors find that it is $\beta\beta$-dibenzylhydroxylamine, and attribute its formation to the setting free of a small quantity of hydroxylamine during the reaction. A. R. L.

Spectrophotometric Investigation of Salts of Aromatic Bases. By L. Meyer (*Zeit. physikal. Chem.*, **11**, 426—428).—A note to the paper by Weigle on the above subject (this vol., i, 333). The author shows that if the rosaniline salts are regarded not as hydrochlorides of amines, but as chlorides of amido-alcohols, the results of Weigle's investigations would still be in keeping with this view. H. C.

Constitution of the Mauveïnes. By O. Fischer and E. Hepp (*Ber.*, **26**, 1194—1196).—The simplest mauveïne, termed by Perkin pseudomauveïne and by the authors phenomauveïne, is identical with the violet induline obtained by the action of nitrosoaniline on aniline hydrochloride, and also with B_2-4-anilidoinduline from diphenylmetaphenylenediamine and nitrosoaniline (compare this vol., i, 335); the corresponding dimethylphenomauveïne is the "indazine" prepared from nitrosodimethylaniline and diphenylmetaphenylenediamine, whilst the mauvindone, $C_6H_3O\langle\begin{smallmatrix}N\\NPh\end{smallmatrix}\rangle C_6H_3\cdot NHPh$, is formed from nitrosophenol and diphenylmetaphenylenediamine, and closely resembles the rosindones. The great similarity in properties between the mauveïnes and safranines renders it probable that the amido-groups are symmetrically distributed in both classes of compounds. The authors have hitherto failed in preparing specimens of safranine bases free from oxygen. J. B. T.

Action of Chlorine on Isonitrosoketones. By L. Claisen and O. Manasse (*Annalen*, **274**, 95—98).—In the preparation of isonitrosoketones by treating the ketone with amylic nitrite and nitrous acid (Abstr., 1889, 585), an excess of hydrochloric acid must be avoided or a chlorinated derivative is obtained. From acetophenone, for example, there is produced *chlorisonitrosoacetophenone*,

$$COPh\cdot CCl{:}NOH;$$

it forms nacreous plates, melts at 132°, and yields benzoic acid on decomposition with alkalis. In an analogous manner, by chlorinating acetone, Glutz's chlorisonitrosoacetone, $COMe\cdot CCl{:}NOH$, melting at 109°, is formed. A. R. L.

Aromatic Alkyl Ketones. By A. Claus (*J. pr. Chem.* [2], **47**, 420—425; compare this vol., i, 162).—*Orthocymylmethylketoxime* [Pr^a : Me : $CMe\cdot NOH$ = 3 : 4 : 1] is a viscid, yellow oil.

Orthocymylcarboxylic acid [Me : Pr$^{\alpha}$: COOH = 1 : 2 : 4] is distilled over with steam from the product of the oxidation of orthocymyl methyl ketone (Abstr., 1890, 770) by dilute permanganate solution in the cold; it forms small, colourless crystals, melts, but not sharply, at 89°, dissolves in the usual solvents, and sublimes. The *barium* salt (with $2H_2O$), the *calcium* salt (with $2H_2O$), and the *silver* salt were prepared.

Orthocymylacetamide [Me : Pr$^{\alpha}$: CH_2·$CONH_2$ = 1 : 2 : 4] crystallises in white needles, and melts at 112°; by hydrolysis, it yields *methylpropylphenylacetic acid* [Me : Pr : CH_2·COOH = 1 : 2 : 4], a viscid, yellow oil; the *calcium* and *barium* salts (each with 1 mol. H_2O) have been prepared.

Orthocymyl ethyl ketone [Me : Pr$^{\alpha}$: COEt = 1 : 2 : 4] is a colourless liquid of aromatic odour which boils at 266—269°. *Orthocymyl propyl ketone* [Me : Pr$^{\alpha}$: COPr$^{\alpha}$ = 1 : 2 : 4] is a colourless oil which boils at 285—287°. The *ketoximes* of these two ketones are viscid, uncrystallisable oils. A. G. B.

Isomeric Amidobenzoic acids. By O. de Coninck (*Compt. rend.*, **116**, 758—760).—The coefficients of solubility of the three isomerides in pure ether are as follows:—

	Ortho-.	Meta-.	Para-.
At 2·7°	1·0840	0·1700	0·6414
At 5·6—6·8°	1·6050	0·1810	0·8210

and in alcohol of 90°

At 3·0°	0·8130	0·1790	0·8400
At 9·6°	1·0700	0·2200	1·1300

The coefficient of solubility of metamidobenzoic acid in dilute ethyl alcohol (1 : 3) at 14·9° is 0·0726, at 16·8, 0·0734; in alcohol of 90° at 12·5°, 0·2920; in methyl alcohol at 10·5°, 0·4046; in acetone at 11·3°, 0·6215; in methylic iodide at 10°, 0·0040; in ethylic iodide at 0°, 0·0016; in chloroform at 12°, 0·0070; in bromoform at 8°, traces; in terebenthene at 10°, traces; in water at 0°, 0·0403; at 20°, 0·0686: at 28°, 0·0820; at 38°, 0·1010; at 48·1°, 0·1396; at 54°, 0·1580; at 67°, 0·2870. A table is given showing the coefficient of solubility of the acid in water at various temperatures between 0·0° and 67·0°. Metamidobenzoic acid is easily soluble in methyl alcohol and in acetone, but almost insoluble in alcohol derivatives and in aromatic hydrocarbons. C. H. B.

Alkylic Benzeneazocyanacetates and their Analogues. By A. Haller and E. Brancovici (*Compt. rend.*, **116**, 714—718).—Ethylic and methylic benzeneazocyanacetates, after being treated with alkali hydroxides at the ordinary temperature, show considerable differences in appearance and properties. This fact has already been observed by Kruckeberg in the case of the ethylic salt.

Ethylic benzenazocyanacetate α, obtained by the action of an alcoholic solution of ethylic sodiocyanacetate on a cooled aqueous solution of diazobenzene chloride, dissolved in excess of potassium

hydroxide, precipitated by means of sulphuric acid and crystallised from alcohol, forms yellow needles melting at 124—125°, and having all the properties previously described.

If the product is crystallised from alcohol or benzene without being previously dissolved in potassium hydroxide solution, it forms needles which melt at temperatures varying from 104° to 120°. After dissolving in potash solution and reprecipitating with acid, however, the product melting at 124—125° is always obtained.

Ethylic benzeneazocyanacetate β, obtained by Kruckeberg by exactly neutralising an acetic or hydrochloric acid solution of the α-modification, or by heating the α-modification at 130°, is always formed at the same time as the α-variety, although in much smaller quantity, and when the crude product is repeatedly crystallised from alcohol, the β-modification accumulates in the mother liquors. It is also obtained by incompletely neutralising an alkaline solution of the α-modification, or by heating the latter for several hours in a xylene solution, or for several days at 100°. The β-modification crystallises from alcohol in rhomboidal tables melting at 85°; it is much more soluble than the α-modification in most of the ordinary solvents. From benzene it crystallises in hexagonal lamellæ, which are transparent while in the liquid, but become opaque in contact with air. When dissolved in potassium hydroxide and reprecipitated with excess of acid, it is converted into the α-modification.

Ethylic benzoylbenzeneazocyanacetate is obtained by the action of benzoic chloride on a solution of the α-modification of the preceding compound in sodium hydroxide; it crystallises from alcohol in white needles melting at 158°. *Ethylic methylbenzeneazocyanacetate* is obtained by the action of methylic iodide on either form of the first compound; it crystallises in pale-yellow prisms melting at 57°. *Ethylic sodiobenzeneazocyanacetate* is obtained by evaporating a mixture of sodium ethoxide and ethylic benzeneazocyanacetate in molecular proportion. It forms a crystalline, yellow powder soluble in water or in alcohol, but insoluble in alkalis. When dried in the air, it has the composition $C_{11}H_{10}N_3O_2Na + 2H_2O$, but loses part of its water in a vacuum.

Methylic benzeneazocyanacetate, obtained in the same way as the ethylic salt, forms an α-modification which melts at 141°, and is very slightly soluble in benzene, but more soluble in boiling alcohol, which partially converts it into the β-modification. The latter crystallises in yellow lamellæ or needles melting at 115°.

Methylic methylbenzeneazocyanacetate melts at 121°, and *methylic benzoylbenzeneazocyanacetate* crystallises from benzene in slender, white needles melting at 147°.

These compounds do not give reactions characteristic of hydrazones. The differences between the α- and β-modifications are most probably due to stereoisomerism. C. H. B.

Action of Hydroxylamine on Orthobenzoylbenzoic acid. By F. H. Thorp (*Ber.*, **26**, 1261—1263).—When orthobenzoylbenzoic acid is heated at 130° with hydroxylamine hydrochloride in absolute alcohol, there is obtained not an oxime, but phthalanilic acid, formed

from the oxime by a molecular transformation similar to that observed by Beckmann (Abstr., 1886, 618; 1887, 826). When this acid is sublimed, it loses water and yields phthalanil, $C_6H_4<^{CO}_{CO}>NPh$, which crystallises in long needles, melts at 203°, and is hydrolysed into phthalic acid and aniline hydrochloride by heating at 130° with strong hydrochloric acid. *Orthobenzoylbenzoic acid oxime*,

$$NOH{:}CPh{\cdot}C_6H_4{\cdot}COOH,$$

may, however, be obtained by allowing the acid to remain with hydroxylamine hydrochloride in dilute alcohol for a long time at the ordinary temperature, and finally warming the mixture on the water-bath. It forms long needles melting at 159—160°, and, when hydrolysed, yields the same products as phthalanil. C. F. B.

Homoterephthalic acid. By M. Fileti and G. Baldracco (*J. pr. Chem.* [2], **47**, 532—534).—The authors have prepared homoterephthalic acid by the hydrolysis of paracyanobenzyl cyanide (Mellinghoff, Abstr., 1890, 239), and find that, when thus prepared, it is in every respect identical with the homoterephthalic acid obtained by oxidising homocumic acid (Abstr., 1891, 1057), melting at 237—238°, not 285—288° as given by Mellinghoff. During the hydrolysis a substance, sparingly soluble in water, was isolated in the form of a crystalline powder melting at 281°. A. G. B.

Ethylic Phthalocyanacetate. By P. T. Muller (*Compt. rend.*, **116**, 760—763).—The white product melting at 175°, obtained by the action of phthalic chloride on ethylic sodiocyanacetate (Abstr., 1891, 1337), is a mixture of two ethylic phthalocyanacetates, the one melting at 140—141°, the other at 190—192°. They can be separated by fractional crystallisation from benzene or chloroform, in which the more fusible compound is the more soluble. Apart from differences in melting point and solubility, the two modifications have the same properties, and they are, undoubtedly, stereoisomerides.

Ammonia converts ethylic phthalocyanacetate into symmetrical phthalamide at the ordinary temperature, and this melts at 219° with evolution of ammonia and formation of phthalimide. If only a small quantity of ammonia acts on the phthalocyanacetate, phthalimide melting at 228° is obtained at once. With a benzene solution of phenylhydrazine, ethylic phthalocyanacetate yields a dihydrazone melting at 149°: it has the constitution

$$C_6H_4<^{C(N{\cdot}NHPh)}_{C(N{\cdot}NHPh)}>C(CN){\cdot}COOEt.$$

Ethylic phthalocyanacetate dissolves very slowly, but completely, in sodium carbonate solution, and, if the liquid is treated with excess of dilute sulphuric acid, *ethylic orthocarboxybenzoylcyanacetate*, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}CH(CN){\cdot}COOEt$, is precipitated, and can be crystallised from ether; it melts at 121—122°, and, when boiled with water, yields phthalic acid and ethylic cyanacetate. It is a bibasic acid, and can be titrated with sodium hydroxide solution, using

phenolphthaleïn as indicator; it yields a white, amorphous diargentic salt. A whole series of alkyl hydrogen salts of this compound can be obtained by the action of ethylic phthalocyanacetate on solutions of sodium alkyl oxides in the corresponding alcohols. They have the general formula $COOR{\cdot}C_6H_4{\cdot}CO{\cdot}CH(CN){\cdot}COOEt$, and are insoluble in water, but dissolve in the ordinary organic solvents. They are monobasic acids, and can be titrated with sodium hydroxide solution, using phenolphthaleïn as indicator. Their lead salts are white, silver salts white or rose-coloured, and copper salts pale green. With ferric chloride, they yield a reddish-brown precipitate which dissolves in ether forming a beautiful red solution. This reaction is characteristic of the group $CO{\cdot}CH(CN){\cdot}COOEt$. The *methylic* salt melts at 64—65°, its *silver* salt is white; the *ethylic* salt is viscous, and its silver salt is rose-coloured; the *propylic* salt melts at 69—70°, and its *silver* salt is reddish; the *benzylic* salt is crystalline, and melts at 74°.

The above alkylic salts, when boiled with a large excess of water, yield *orthocyanacetophenonecarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CN$, a crystalline powder melting at 136—138°.

Almost all these reactions are quantitative. Ethylic phthalocyanacetate sometimes behaves as a symmetrical, sometimes as an unsymmetrical compound. It would seem that certain parts of the molecule have a degree of mobility such that, under different conditions, it can take up the orientation required to produce at once the most stable molecule, which is sometimes symmetrical, sometimes unsymmetrical. C. H. B.

Dihydromethylketole. By E. Bamberger and E. A. Zumbro (*Ber.*, **26**, 1285—1291).—Dihydromethylketole, $C_6H_4{<}^{CH_2}_{NH}{>}CHMe$, or methyldihydroindole, is, as the sequel shows, precisely analogous in chemical character to tetrahydroquinoline, $C_6H_4{<}^{CH_2{\cdot}CH_2}_{NH_2{\cdot}CH_2}{>}$; this character is therefore independent of the length of the side ring, and we have here a case of "alicyclic homology" comparable with the homology of fatty hydrocarbons. This is not the case with the corresponding non-hydrogenised substances; indole, for example, behaves very differently from quinoline.

Diazoamidodihydromethylketole, $C_6H_4{<}^{CH_2}_{N(N_2Ph)}{>}CHMe$, is formed from diazobenzene and dihydromethylketole. It crystallises in long, hard, yellowish, glassy, monoclinic (?) prisms, melts at 51·5°, and exhibits the typical reactions of diazoamido-compounds; in alcoholic solution, acids transform it into an isomeric red azo-dye.

Hydromethylketoleparazobenzenesulphonic acid,

$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3{<}^{CH_2}_{NH}{>}CHMe,$$

is formed when hydromethylketole is mixed with diazosulphanilic acid. It is obtained in two forms: as violet needles, insoluble in water, and melting above 260°, and as a green mass with red streak, soluble in water. The first variety is formed in larger amount in

concentrated solution and when the free base is used; the second in dilute, slightly acid solution. Both varieties, when heated with hydrochloric acid and stannous chloride, yield sulphanilic acid and *paramidodihydromethylketole*, $NH_2 \cdot C_6H_3 < \begin{matrix} CH_2 \\ NH \end{matrix} > CHMe$; the latter forms white, glassy needles melting at 93·5°: its *hydrochloride*, white, crystalline flakes. Like paramidotetrahydroquinoline, the base itself yields the colour reactions of paraphenylenediamine. C. F. B.

Indoxazen Derivatives. By V. Meyer, O. List, J. Marcusson, and W. A. Bone (*Ber.*, **26**, 1250—1257; compare Abstr., 1892, 992, and this vol., i, 94, 35).—Phenylindoxazen, $C_6H_4 < \begin{matrix} CPh \\ O \end{matrix} > N$, may be prepared from orthonitrobenzophenone oxime by boiling it with aqueous soda, sodium nitrite being also formed.

When orthonitrophenylglyoxylic acid oxime is boiled with water, carbonic anhydride is evolved, and orthonitrobenzonitrile is formed. If aqueous sodium carbonate be used, the nitro-group is displaced by hydroxyl, and salicylonitrile is produced: whilst if aqueous soda is used, the cyano-group is also attacked and hydrolysed, and salicylic acid is formed.

Similarly, if nitro-orthochlorobenzaldoxime is boiled with aqueous soda, nitrosalicylic acid is formed, whilst if aqueous sodium carbonate is used, *nitrosalicylonitrile* is produced; the latter may also be obtained by nitrating salicylonitrile with concentrated nitric acid at 15°; it forms yellow needles melting at 190°. If fuming nitric acid is used, a *dinitrosalicylonitrile* [$CN : OH : (NO_2)_2 = 1 : 2 : 3 : 5$] is formed; it crystallises in yellow tables melting at 175°.

Meta- and para-bromobenzophenone oximes yield no substances analogous to the indoxazen obtained from the ortho-derivative.

C. F. B.

Preparation of Benzidine Sulphate. By H. Teichmann (*Zeit. angw. Chem.*, 1893, 67).—A mixture of nitrobenzene (100 grams) sodium hydroxide solution (sp. gr. 1·4; 80 grams) and water (500 c.c.) is heated in a reflux apparatus on the water-bath; zinc-dust (160 grams) is then introduced in small portions; during the addition, which extends over 6—8 hours, the mixture is agitated. When cold, the product is gradually poured into hydrochloric acid (sp. gr. 1·2; 1500 c.c.), which should be free from arsenic, the temperature being kept low by the addition of ice. After this, the liquid is heated to boiling by passing in a current of steam, and it is filtered from resinous matter while hot. The hot filtrate is then treated with a saturated solution of sodium sulphate, whereby almost the whole of the benzidine is precipitated as sulphate. It is collected, washed with water, and dried, when it is obtained in the form of a greyish-blue powder; the yield is 90 per cent. of the weight of nitrobenzene employed, and the product contains 2·5 per cent. of ash. About 5 grams of aniline is driven over by passing a current of steam into the reduction product, but only a relatively small quantity of diphenylamine is formed.

A. R. L.

Preparation of Benzidine. By E. ERDMANN (*Zeit. angw. Chem.*, 1893, 163—164).—Commenting on Teichmann's method (last abstract), the author describes a process for the preparation of benzidine on a large scale which he states is quicker, and gives a good yield. A mixture of nitrobenzene (2 kilos.), sodium hydroxide solution (40° B., 6 litres), water (2 litres), and alcohol (1 litre) is introduced into an earthenware cylinder furnished with a side tube, and a lid having a hole to admit an iron or wooden mixer. The alcohol is not absolutely necessary, but the reaction proceeds with greater regularity when it is used, and less aniline is formed. The side tube is attached to a condenser, and zinc-dust (3·4 kilos.) is introduced in small portions through a tube issuing from the lid. An energetic reaction soon sets in, and a mixture of alcohol and nitrobenzene distils over, which is repeatedly returned. The addition of zinc-dust is so regulated that the mixture does not froth over, and it is kept in agitation with the mixer; when these precautions are neglected, the reaction may become sufficiently violent to cause explosion; the reduction is complete in 2½ hours. The product is allowed to cool, and on the following day diluted with water and thrown upon a sieve, which allows the zinc oxide to pass through, but retains the crystals of hydrazobenzene; the hydrazobenzene may also be isolated by dissolving the zinc oxide at 10—15° in concentrated hydrochloric acid (18 litres). The yield is hydrazobenzene 1170 grams, benzidine 128 grams, and aniline 18 grams. To convert hydrazobenzene into benzidine, 500 grams of the former is boiled with concentrated hydrochloric acid (800 c.c.) and water (1 litre); the precipitated benzidine hydrochloride is collected, and dilute sulphuric acid added to the filtrate as long as a precipitate falls, which is collected. The filtrate is rendered faintly alkaline, the aniline driven over, and the semi-oily residue of diphenylamine collected, converted into sulphate, and further purified. The diphenylamine represents 8—10 per cent. of the hydrazobenzene employed. The yield of benzidine does not exceed 50 per cent. of the weight of nitrobenzene reduced. Boiling water dissolves 0·011 part, and cold water 0·0004—0·0005 part of benzidine. A. R. L.

Formation of Acridine Dyes. By R. MÖHLAU and E. FRITZSCHE (*Ber.*, **26**, 1034—1044).—*Hexamethyltriamidophenylacridine*, $C_{25}H_{28}N_4$, is prepared by the action of hydrochloric acid on nitrosodimethylaniline hydrochloride and dimethylaniline; the addition of paraformaldehyde is advantageous; the mother liquor contains dimethylamine, paramidophenol, and chloroparamidophenols. The compound has been previously described (*Ber.*, **16**, 2729) as "rubifuchsine," $C_{16}H_{19}N_3$; it is readily soluble in dimethylaniline, and crystallises in stellate groups of golden, flat needles, or plates, which melt at 270°. On distillation, the greater part of the compound decomposes into paraphenylenediamine and dimethylparatoluidine. The *hydrochloride*, $C_{25}H_{28}N_4,2HCl$, is deposited in small, light red needles, containing $1H_2O$; on slowly cooling the solution, brownish-red or steel-blue needles are formed, containing $5H_2O$; the anhydrous

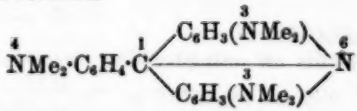
salt is red, and gives a colourless solution with concentrated hydrochloric acid or sulphuric acid.

On reducing the dye with zinc-dust in acetic acid solution, a colourless, readily oxidisable leuco-derivative is formed; in hydrochloric acid solution, the base is resolved into paraphenylenediamine, dimethylparatoluidine, and, probably, benzene.

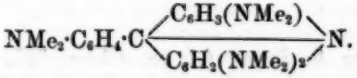
Octomethyltetramidophenylacridine, $C_{27}H_{33}N_5$, is obtained together with the hexamethyl compound, and is readly prepared by the action of hydrochloric acid on a mixture of paraformaldehyde, dimethylaniline, and nitrosodimethylaniline hydrochloride; the base crystallises from alcohol in yellow plates, melts at 229°, and in small quantities distils without decomposition. The compound gives no coloration with concentrated hydrochloric acid or sulphuric acid; on continuous dilution, the solution becomes yellow, then orange-red. The *hydrochloride*, $C_{27}H_{33}N_5,2HCl + 5H_2O$, crystallises in lustrous rhombic plates or prisms, which appear dark green by reflected light and deep red in transmitted light. No quinone dichlorodiimide is formed by the action of calcium hypochlorite.

Like the hexamethyl derivative, the octomethyl compound readily forms a leuco-base, and on reduction in hydrochloric acid solution is resolved into dimethylparatoluidine and paramidodimethylaniline, together with other substances which could not be isolated.

In all acridine derivatives hitherto prepared, the basic groups occupy the para-position relatively to the carbon atom which links the benzene nuclei, but in the preceding compounds the basic groups are in the meta-position relatively to the carbon atom, and in the para-position relatively to the nitrogen atom of the group :C·N:; this probably accounts for the absence of fluorescence, and for the comparative instability of the compounds. The formation of the bases is explained by the assumption that part of the nitrosodimethylaniline is decomposed with the production of formic acid, whilst another portion combines with some of the dimethylaniline to form dimethylphenylene-green, $NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_3{\cdot}NMe_2$; the latter compound then condenses with the formic acid and the remaining dimethylaniline; hexamethyltetramidophenylacridine is therefore represented by the formula



and the octomethyl derivative by the formula



J. B. T.

Xanthydrol. By R. Meyer and E. Saul (*Ber.*, **26**, 1276—1279). —*Xanthydrol*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH{\cdot}OH$, may be obtained by reducing xanthone in alcoholic soda solution with sodium amalgam. It forms tiny, colourless needles, does not melt at a definite temperature, and

with strong sulphuric acid, gives a yellow solution, with a green fluorescence. It is very readily oxidised to xanthone, which is formed when it is dried at rather over 100°, and also when attempts are made to condense it to diphenylenephenylmethane oxide. In one such attempt, however, when xanthydrol and benzene were heated with phosphoric anhydride, a small quantity of diphenylenemethane oxide, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH_2$, was formed. When xanthydrol is boiled with light petroleum, it yields the *ether* $(O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH)_2O$ as nodular aggregates, also obtainable as short, lustrous crystals, which melt at about 200°. This substance is identical with that prepared by Richter (Abstr., 1884, 325), by reducing xanthone in alcoholic soda solution with sodium amalgam, and recrystallising the product from chloroform. He supposed it to be a compound of xanthone with diphenylenemethane oxide, but he really obtained xanthydrol in the first place, and unknowingly transformed it into its ether by crystallisation from chloroform. C. F. B.

Colouring Matters of the Triphenylmethane Series. By K. Hofmann (*Ber.*, **26**, 1139—1146).—By heating pyrogallol and benzaldehyde with zinc chloride, a brick-red substance is obtained, which has not the properties of an aurine dye; its constitution is perhaps represented by $O_2\ll\begin{matrix}C_6H_2(OH)\\C_6H_2(OH)\end{matrix}>CHPh$, a compound,

$$OH\cdot C_6H_3:O_2:C_6H_3\cdot OH,$$

having been possibly formed as an intermediate product. With acetic anhydride and sodium acetate, this substance yields a brick-red diacetyl derivative; with a larger excess of anhydride and longer boiling, a reddish triacetyl derivative, $O_2\ll\begin{matrix}C_6H_2(OAc)\\C_6H_2(OAc)\end{matrix}>CPhAc$?.

When pyrogallol and benzaldehyde are heated with fuming hydrochloric acid at 100° in an open beaker, a red substance is obtained which has the properties of an aurine dye, and may be represented by the formula $O<\begin{matrix}CPh\text{——}C_6H_2(OH)_2\\|\qquad\qquad|\\C_6H_2(OH)\cdot O\end{matrix}$. With acetic anhydride and sodium acetate, it yields an orange-yellow triacetyl derivative which melts at 177°, and may be regarded as $O_2\ll\begin{matrix}C_6H_2(OAc)\\C_6H_2(OAc)\end{matrix}>CPh\cdot OAc$. The formulæ suggested in the paper are, of course, tentative only. C. F. B.

Auramines. By A. Stock (*J. pr. Chem.* [2], **47**, 401—413).—*Acetylphenylauramine zinc thiocyanate*, $(C_{25}H_{25}N_3)CNS,Zn(CNS)_2 + 4H_2O$, was prepared by acetylising phenylauramine, treating the aqueous solution with potassium thiocyanate and zinc chloride, and salting out. It is a dark powder with a metallic lustre; acids and alkalis decompose it with formation of tetramethyldiamidobenzophenone, aniline, and acetic acid.

Methylphenylauramine hydrochloride,

$$C_6H_4<\begin{matrix}NMe_2Cl\\ C(C_6H_4\cdot NMe_2)\cdot NMePh,HCl\end{matrix},$$

obtained by heating methylaniline, tetramethyldiamidobenzophenone, and phosphorus oxychloride together in benzene, is a bright red, amorphous powder, and dissolves in chloroform, alcohol, and water; in the last two solvents it soon becomes decolorised, and, in the aqueous solution at all events, decomposed into methylaniline and tetramethyldiamidobenzophenone. The *zincochloride* was isolated. By passing dry ammonia into a chloroform solution of methylphenylauramine hydrochloride, methylaniline and auramine hydrochloride are produced.

Diphenylauramine results from the condensation of dimethylamidobenzodiphenylamide with dimethylaniline; its *zincochloride* was prepared.

Pentamethyleneauramine is obtained by the action of piperidine on tetramethyldiamidobenzophenone chloride. The *zincochloride* was prepared.

From this investigation, the author deduces the following generalisations concerning auramines: 1. They are derived from the triphenylmethane colouring matters by the substitution of an amido-group for one of the benzene nuclei. 2. Their colour depends on the basicity of the entering amido-residue; when this is strong, they are yellow, and as the basicity becomes more feeble, they pass into red; by the introduction of an acid residue, the colour becomes violet-blue. 3. The di-substituted auramines are decomposed by acids and alkalis into ketones and amines. 4. Dry ammonia eliminates the alkyl amido-residue as a secondary amine, and substitutes NH_2 for it. Aqueous ammonia behaves partly in this way and partly as an alkali (see above). A. G. B.

Action of Phenylhydrazine on Lactones. By R. Meyer and E. Saul (*Ber.*, **26**, 1271—1276).—Phthalide, as W. Wislicenus found (Abstr., 1887, 489), when heated with phenylhydrazine on the water-bath, yields an additive product, $N_2H_2Ph\cdot CO\cdot C_6H_4\cdot CH_2\cdot OH$. Diphenylphthalide and fluoran yield no compounds under these circumstances, but if boiled with phenylhydrazine they yield the condensation products, $CO<\begin{matrix}C_6H_4-\\ N_2HPh\end{matrix}>CPh_2$ and $CO<\begin{matrix}C_6H_4-\\ N_2HPh\end{matrix}>C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>O$ respectively. Phthalide itself yields no such derivative under these circumstances, but this is not surprising, since it decomposes at a temperature considerably below the boiling point of phenylhydrazine. The hydrazone of diphenylphthalide crystallises in colourless prisms melting at 230—231°, and, like diphenylphthalide itself, exhibits no fluorescence when dissolved in strong sulphuric acid. The hydrazone of fluoran crystallises in colourless needles melting, with partial decomposition, at 285—287°; like fluoran itself, it gives a fluorescent solution with strong sulphuric acid. C. F. B.

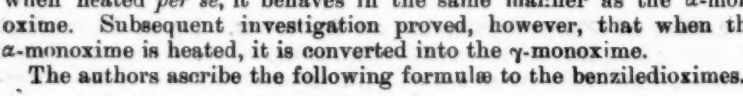
Hydroximido-derivatives: Benzileoximes. By E. Beckmann and A. Köster (*Annalen*, **274**, 1—36; compare Abstr., 1889, 1067).—The formation of benzoic acid and ammonia from α-benzilemonoxime has been already described (*loc. cit.*). Adopting the hypothesis of Hantzsch and Werner to explain the isomerism of the benzileoximes, the authors represent the α-monoxime by the formula $Ph\cdot\overset{\overset{N\cdot OH}{\|}}{C}\cdot COPh$; consequently the γ-monoxime must be represented by the alternative formula $Ph\cdot\overset{\overset{OH\cdot N}{\|}}{C}\cdot COPh$. These views, which it is urged are justified by the results to be described, are in opposition to those of Hantzsch and Werner (Abstr., 1890, 350); compare also Claus (Abstr., 1892, 50).

When the α-monoxime is dissolved in ether and treated with phosphoric chloride, an oil, probably CPhCl:N·COPh, is obtained, which decomposes on distillation into a mixture of benzonitrile and benzoic chloride, and yields dibenzenylazoxime on treatment with hydroxylamine. The α-monoxime decomposes when heated above 200° into benzonitrile and benzoic acid (see below).

On treating an ethereal solution of γ-benzilemonoxime with phosphoric chloride and subsequently shaking the product with an excess of soda solution, *benzoylformanilide*, NHPh·CO·COPh, is formed; it crystallises in golden-yellow needles, melts at 63°, and decomposes when heated with glacial acetic acid at 200° into benzoic acid, acetanilide, and formic acid.

It yields an *oximido*-compound, NHPh·CO·CPh:NOH, which melts at 205—206°, is isomeric with the benziledioximes, and forms an *acetyl* derivative melting at 140°. Benzoylformanilide was also prepared by treating aniline benzoylformate with phosphoric chloride. When the γ-monoxime is heated with concentrated sulphuric acid, it yields benzoic acid, aniline, and sulphanilic acid, and when heated *per se*, it behaves in the same manner as the α-monoxime. Subsequent investigation proved, however, that when the α-monoxime is heated, it is converted into the γ-monoxime.

The authors ascribe the following formulæ to the benziledioximes.



α-Benziledioxime. β-Benziledioxime. γ-Benziledioxime.

The α-dioxime yields the anhydrides, dibenzenylazoxime, and isodibenzenylazoxime (Abstr., 1889, 1067). The β-dioxime is converted into oxanilide by phosphoric chloride (*loc. cit.*), and when treated with sulphuric acid, oxanilideparasulphonic acid is formed. The γ-dioxime, on treatment with phosphoric chloride, yields phosphorus oxychloride, or sulphuric acid, dibenzenylazoxime and benzoylphenylcarbamide, or their decomposition products. Under specific treatment, the γ-dioxime is converted into the α-dioxime, and under other circumstances, it is converted into the β-dioxime (compare Auwers and Meyer, Abstr., 1889, 713). Both the α- and the γ-dioximes

yield the normal anhydride of melting point 94°, but whilst an anhydride is only obtained from the γ-monoxime by the hydrolysis of its acetyl derivative, the α-dioxime is converted into anhydrides under the circumstances mentioned above. A. R. L.

Constitution of β-Hydroxynaphthoic acid (m. p. 216°). By J. Schmid (*Ber.*, **26**, 1114—1121).—This acid does not, as Hosaeus states (this vol., i, 355), yield a benzenetricarboxylic acid when oxidised with permanganate, nor does it, as he concludes, contain the hydroxyl and carboxyl groups in different rings. For a number of reasons, which it is impossible to reproduce here, the constitution of an orthohydroxynaphthoic acid is assigned to it, $OH{\cdot}C_{10}H_6{\cdot}COOH$ [OH : COOH = 2 : 3]. When oxidised with 10 per cent. alkaline permanganate on the water-bath, it yields nothing but phthalic acid. When sulphonated with concentrated sulphuric acid, it forms two isomeric *β-hydroxysulphonaphthoic acids*

$$[OH : COOH : SO_3H = 2 : 3 : 1'] \text{ and } [2 : 3 : 3'],$$

of which the former yields well-crystallised normal salts, the latter well-crystallised acid salts, but very soluble normal salts which crystallise with difficulty. When these acids are fused with potash, they yield the corresponding *dihydroxynaphthoic acids* $[(OH)_2 : COOH = 2 : 1' : 3]$ and [2 : 3′ : 3], both crystallising in yellow needles, but melting, the former at 265—267°, the latter, with decomposition, at 225—228. When either of the above-mentioned β-hydroxysulphonaphthoic acids, or β-hydroxynaphthoic acid itself, is heated at 100—140° with fuming sulphuric acid (containing 24 per cent. SO_3), *β-hydroxydisulphonaphthoic acid*

$$[OH : COOH : (SO_3H)_2 = 2 : 3 : 1' : 3']$$

is formed; this, when oxidised with permanganate, yields the same disulphophthalic acid as is obtained by the oxidation of the trisulphonic derivative of β-naphthol. When fused with soda, it yields *dihydroxysulphonaphthoic acid* $[(OH)_2 : COOH : SO_3H = 2 : 1' : 3 : 3']$, which forms pale yellow needles; the barium hydrogen salt crystallises from hot water with $2H_2O$. This acid is very stable towards soda; only when heated with potash at 310—320°, was an acid obtained, forming yellow needles melting at 255—257° (? *trihydroxynaphthoic acid* $[(OH)_3 : COOH = 2 : 1' : 3' : 3]$). β-Hydroxydisulphonaphthoic acid, when heated at 240—280° with strong aqueous ammonia, yields *β-amidodisulphonaphthoic acid*

$$[NH_2 : COOH : (SO_3H)_3 = 2 : 3 : 3' : 1'],$$

forming white needles, and giving a yellowish-green fluorescence in alkaline solution. When this acid is heated with soda at 200—240°, it yields *β-amidohydroxysulphonaphthoic acid* $[NH_2 : COOH : SO_3H : OH = 2 : 3 : 3' : 1']$, which crystallises in tufts of white prisms. When in this acid the NH_2 is displaced by OH by means of the diazo-reaction, the product is the dihydroxysulphonaphthoic acid described above. C. F. B.

Constitution of β-Hydroxynaphthoic acid (m. p. 216°). By M. Schöpff (*Ber.*, **26**, 1121—1124).—As, contrary to Hosaeus' statement, β-hydroxynaphthoic acid (m. p. 216°) can be converted into a naphthacridine, it must be an *ortho*-hydroxynaphthoic acid. If β-anilidonaphthoic acid is heated with zinc chloride, phenonaphthacridone (melting at 242—244°) is formed, as already stated (Abstr., 1892, 1477), and this, when heated with zinc-dust in a current of hydrogen, yields a dihydrophenonaphthacridine melting at 167—168°. The acridone, when heated with dilute hydrochloric acid at 180°, is converted into an isomeride, melting above 290°, and insoluble in alkalis, $C_{10}H_{16}<\begin{matrix}N\text{——}\\|\\C(OH)\end{matrix}>C_6H_4$ (?); this substance is obtained from β-anilidonaphthoic acid directly by heating it with dilute hydrochloric acid at 180°, and also from β-hydroxynaphthoic anilide by heating it with zinc chloride at 230—250°.

The substance mistaken by Hosaeus for benzenetricarboxylic ("hemimellitic") acid was probably 1 : 2-*carboxyphenylglyoxylic acid*, $COOH\cdot C_6H_4\cdot CO\cdot COOH$. This is readily obtained by oxidising β-hydroxynaphthoic acid with alkaline permanganate at the ordinary temperature. The acid itself, obtained by extraction with ether, forms an oil which gradually solidifies to a mass of needles. By warming the solution with phenylhydrazine hydrochloride at 80°, *phenylphthalazonecarboxylic acid*, $CO<\begin{matrix}C_6H_4\\N_2Ph\end{matrix}>C\cdot COOH$, is obtained, forming colourless needles melting at 221—222°, and doubtless identical with the substance melting at 214—215° obtained by Henriques from a compound formed by oxidising β-naphthol with alkaline permanganate at the ordinary temperature (Abstr., 1888, 842).

C. F. B.

β-Hydroxynaphthoic acid (m. p. 216°). By R. Hirsch (*Ber.*, **26**, 1176—1179; compare Hosaeus, this vol., i, 355; Schmid and Schöpff, preceding abstracts).—β-Hydroxynaphthoic acid (1 part) is treated with sulphuric acid (2 parts) at 75°, the product is converted into the calcium salt, and, on evaporation, crystals (A) are deposited; the mother liquor, on concentration, yields a second pulverulent salt (B), which is separated from the hot solution; on further evaporation, the filtrate deposits crystals of the compound A.

The salt A is soluble in about 14 parts of water at 100°, and crystallises with $5H_2O$; the *potassium salt* is deposited from alcohol in prismatic aggregates, and becomes yellow when heated, but on cooling the colour disappears. The sulphonic acid is prepared from the calcium salt, and is identical with the compound prepared by Hosaeus (*loc. cit.*); it gives a violet-blue coloration with ferric chloride, and forms a dye with diazo-compounds.

The salt B dissolves in about 75 parts of water at 100°; the *barium salt* is sparingly soluble; the *potassium*, *sodium*, and *ammonium salts* readily dissolve, and the solutions are slightly fluorescent; they give a violet-blue coloration with ferric chloride, and undergo scarcely any alteration on heating. The *sulphonic acid*

is more sparingly soluble than the isomeric compound, and does not combine so readily with diazo-compounds.

The author considers that the properties of the above compounds prove that in β-hydroxynaphthoic acid the groups occupy the positions 2 : 3; there is no proof that Hosaeus' sulphonic acid is not an ortho-compound, since the hydroxyl would probably exert quite as much influence as the carboxyl on the position of the sulphonic group, but, apart from this, the acid is as likely to be a dis-heteronucleal compound as it is to be a meta- or para-homonucleal derivative. J. B. T.

1 : 1′-Naphthalic acid and its Derivatives. By G. F. JAUBERT (*Chem. Centr.*, 1893, i, 572—573; from *Arch. sci. phys. nat. Genève*, **29**, 141—161).—1 : 1′-Naphthalic acid is prepared by oxidising acenaphthene dissolved in glacial acetic acid (6 parts) with potassium dichromate (12 parts). The oxidation product is precipitated with acid, the precipitate treated with 5 per cent. soda solution, which dissolves the naphthalic acid from the bye-products, and it is finally crystallised from nitric acid (sp. gr. 1·48), from which a portion of the acid separates as anhydride; the remainder of the acid is precipitated by the addition of water. It is converted into the *anhydride*, $C_{10}H_6<^{CO}_{CO}>O$, when heated at 180°; the latter forms white needles, melts at 274°, and is almost insoluble in water, very sparingly soluble in ether, and only slightly so in alcohol. It is not attacked by chlorine, phosphoric chloride, or sulphur dichloride.

The *imide*, $C_{10}H_6<^{CO}_{CO}>NH$, is formed on treating the anhydride with ammonia; it melts at 300°, and may be crystallised from cold concentrated nitric acid.

The *sodium* and *potassium* derivatives were prepared; the *methyl* derivative, $C_{10}H_6<^{CO}_{CO}>NMe$, melts at 205°; the *ethyl* derivative melts at 148°, the *phenyl* derivative at 202°, the *benzyl* derivative at 196·6°, and the *orthotolyl* derivative at 214·2°.

When 1 : 1′-naphthalic anhydride is treated with hydroxylamine, it yields a colourless *oxime*, $C_{10}H_6<^{CO}_{CO}>NOH$, melting at 284°; its *metallic* derivatives are red, brown, or yellow; the *methyl* derivative melts at 211°, and the *ethyl* derivative melts at 160°. An analogue of anthranilic acid is not formed by treating the sodium derivative of the oxime with alcoholic soda.

The *phenylhydrazone*, $C_{10}H_6<^{CO}_{CO}>N_2HPh$, melting at 218·5°, is obtained by treating 1 : 1′-naphthalic anhydride with phenylhydrazine; the *acetyl* derivative melts at 230°, and the *benzoyl* derivative at 230·5°. On reduction with zinc or tin and hydrochloric acid, the hydrazone furnishes hydroxynaphthalide (Abstr., 1892, 864), but experiment failed to produce a compound analogous to phthalide by the reduction of the above-mentioned naphthalimide. A. R. L.

Amidonaphtholsulphonic acids. By F. Reverdin and C. De la Harpe (*Ber.*, **26**, 1279—1284; compare Abstr., 1892, 996).—An *amidonaphtholsulphonic acid* [OH : NH_2 : SO_3H = 1 : 2 : 4 or 1 : 2 : 4′] is obtained by the direct sulphonation of 1 : 2-amidonaphthol, which is itself got by reducing 1 : 2-nitrosonaphthol (best obtained from 1 : 2-hydroxynaphthoic acid and nitrous acid) with stannous chloride. It oxidises on standing in sodium carbonate solution to a violet-black dye, and has all the properties of the 1 : 2 : 4-acid previously described (Abstr., 1892, 996), but may possibly have the 1 : 2 : 4′-constitution. An isomeric acid [OH : NH_2 : SO_3H = 1 : 4 : 3] is obtained by reduction of the nitroso-derivative of 1 : 3-naphtholsulphonic acid or of the azo-dye which this acid yields with diazobenzene chloride. It yields a small quantity of a greenish-brown colouring matter when oxidised.

Amidonaphtholdisulphonic acid [OH : NH_2 : $(SO_3H)_2$ = 1 : 2 : 4 : 3′] is obtained from 1 : 4 : 3′-naphthylaminedisulphonic acid by converting it, by means of the diazo-reaction, into naphtholdisulphonic acid, combining this with diazobenzene chloride, and reducing the product. By the addition of sodium chloride, it can be separated from solution in white needles, probably as the sodium hydrogen salt. When oxidised, it yields a violet-black dye. The isomeric 1 : 2 : 4 : 2′-acid is obtained in a similar manner from 1 : 4 : 2′-naphthylaminedisulphonic acid; also by reducing the nitroso-derivative of 1 : 4 : 2′-naphtholdisulphonic or the compound of diazobenzene chloride with 1 : 2 : 4 : 2′-hydroxydisulphonaphthoic acid; it forms white needles, and, when oxidised, yields a dirty red dye. A third isomeric 1 : 2 : 4 : 1′-acid is obtained by reducing the compound of diazobenzene chloride with the 1 : 4 : 1′-naphtholdisulphonic acid obtained by sulphonating naphthosulphone. It is a well-crystallised substance, and, when oxidised, yields a greenish-black dye. All these disulphonic acids can be diazotised, and the products yield dyes with resorcinol, β-naphthol, and β-hydroxynaphthoic acid, in the last case of a bluish-violet colour. 1 : 4 : 2 : 7-Amidonaphtholdisulphonic acid and the 1 : 2 : 4-monosulphonic acid can be only partially diazotised.

Amidonaphtholsulphonic acid [OH : NH_2 : SO_3H = 2 : 1 : 4′], from 2 : 4′-naphthylaminesulphonic acid, has been shown to be identical with that previously obtained from the naphthylaminesulphonic acid γ- of the Badische Anilin und Soda Fabrik. C. F. B.

Some Benzenesulphonates of the Aromatic Series. By M. Georgescu (*Chem. Centr.*, 1893, i, 302; from *Bull. Soc. Sci. Fiz. Bucuresci*, 1892, 213; compare Abstr., 1891, 49, 202, and 568).—Benzenesulphonic chloride reacts with alizarin, anthrapurpurin, and galleïn, forming the following compounds:—*Alizarin benzenesulphonate*, $C_6H_4{:}C_2O_2{:}C_6H_2(O{\cdot}SO_2Ph)_2$, melting at 182—184°; *anthrapurpurin benzenesulphonate*, $C_6H_5{\cdot}SO_2{\cdot}O{\cdot}C_6H_3{:}C_2O_2{:}C_6H_2(OPh)_2$ (?), melting at 182—186°; *gallein dibenzenesulphonate*,

$$C_6H_4<\begin{matrix}CO{\cdot}C_6H_2(OH){\cdot}(OSO_2Ph)\\CO{\cdot}C_6H_2(OH){\cdot}(OSO_2Ph)\end{matrix}>O,$$

which appears to decompose at 100—120°; and *gallein tetrabenzenesulphonate*, $C_6H_4<\begin{matrix}CO\cdot C_6H_2(O\cdot SO_2Ph)_2\\CO\cdot C_6H_2(O\cdot SO_3Ph)_2\end{matrix}>O$, melting at 187—188°.

A. R. L.

Isonitrosocamphor and its Derivatives. By L. Claisen and O. Manasse (*Annalen*, **274**, 71—94).—A better method for the preparation of isonitrosocamphor than that previously given (Abstr., 1889, 619) is described. Sodium in the form of wire is added to an ethereal solution of camphor, and the mixture poured into amylic nitrite cooled by ice; the resulting sodium salt is dissolved in water and decomposed by acetic acid. Isonitrosocamphor crystallises in rhombic prisms, $a : b : c = 0{\cdot}8775 : 1 : 0{\cdot}6361$; it is much more stable than Cazeneuve's nitrosocamphor (Abstr., 1889, 720). The *phenylhydrazone*, $C_8H_{14}<\begin{matrix}C\cdot NOH\\C\cdot N_2HPh\end{matrix}$, forms small, yellow needles, melts at 130°, and has acidic properties; it dissolves in concentrated sulphuric acid with a deep purple colour which changes to blue on the addition of sodium nitrite, and an alcoholic solution gives a dark red coloration on addition of ferric chloride. When isonitrosocamphor is gently heated with fuming hydrochloric acid, it dissolves with ebullition, and camphoramic acid, $NH_2\cdot CO\cdot C_8H_{14}\cdot COOH$, is obtained. This crystallises from boiling water in colourless leaflets, melts at 174—176°, and when heated above its melting point yields camphoric anhydride (not camphoric imide, as stated by Laurent, *Annalen*, **60**, 326). When isonitrosocamphor is heated for some hours on the water-bath with fuming hydrochloric acid, camphoric acid and camphoric imide, $C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>NH$, melting at 244—245° (corr.), are formed (compare Abstr., 1890, 1152).

The preparation and properties of camphororthoquinone have been already described (Abstr., 1889, 619). The yellow solution of the quinone is not decolorised by sulphurous acid, but when the compound is boiled with aqueous alkalis camphoric acid is formed. The phenylhydrazone, $C_8H_{14}<\begin{matrix}C\cdot N_2HPh(\beta)\\CO(\alpha)\end{matrix}$, crystallises in yellowish prisms, and melts at 170—171°; it is identical with the compound obtained by Claisen and Bishop (*Sitzungsber. kgl. Bayer. Akad.*, 1890, 460 and 478) by the action of diazobenzene chloride on hydroxymethylenecamphor.

Amidocamphor, $C_{10}H_{15}O\cdot NH_2$, is obtained by reducing isonitrosocamphor with zinc-dust and acetic acid; it boils at 243—245°, and is probably identical with the compound obtained by Schiff (Abstr., 1880, 891; compare also Kachler and Spitzer, *Monatsh.*, **4**, 567). The *hydrochloride* crystallises in needles, and melts at 223—225°; the *platinochloride* and *nitrite* are crystalline. The *formyl* derivative, $C_{10}H_{15}O\cdot NH\cdot CHO$, melts at 76—77°; the *acetyl* derivative,

$$C_{10}H_{15}O\cdot NHAc,$$

melts at 108°, and the *benzoyl* derivative melts at 140°. A. R. L.

Champacol, a New Camphor. By E. MERCK (*Arch. Pharm.*, **231**, 123).—*Champacol*, $C_{17}H_{30}O$, occurs in champaca-wood, and is obtained from it by steam distillation. It crystallises in long, white, matted needles, has no odour, melts at 86—88°, and can be sublimed. When pure, it is stable, but when impure, it liquefies, and a smell of champaca-wood can be perceived. C. F. B.

Hydroxymethylene Compounds. By L. CLAISEN (*Ber.*, **26**, 1173).—The statement attributed to v. Pechmann (this vol., i, 360), that the methyl derivative of oxymethylenecamphor is an oil, was due to a misapprehension on the part of the author. C. F. B.

Gum Benzoïn from Sumatra. By F. LÜDY (*Arch. Pharm.*, **231**, 43—95).—This substance, which differs from that obtained from Siam, has been very carefully examined. Contrary to previous statements, it is entirely soluble in ether, fragments of wood, of course, excepted. The α-, β-, and γ-resins of earlier investigators are shown to be mixtures of partially hydrolysed cinnamates of benzoresorcinol and resinotannol, the α-resin being the least and the γ- the most hydrolysed; the α- and β-resins can, by boiling with caustic potash, be converted into the γ-resin, which is thus the sole product of the prolonged action of caustic potash on the resin of gum benzoïn. No resin is contained in the uninjured bark; it is formed as a consequence of the injury.

The author summarises his results as follows:—Gum benzoïn (from Sumatra) is soluble in ether, and the dissolved substance yields 0·01 per cent. ash. It contains, besides benzoic acid and cinnamene, (1) benzaldehyde, traces; (2) benzene, traces; (3) vanillin, 1 per cent.; (4) phenylpropylic cinnamate, 1 per cent.; (5) cinnamylic cinnamate, 2—3 per cent.; (6) a mixture of a little *benzoresinol cinnamate* with much *resinotannol cinnamate*, this mixture forming the main constituent of the gum. In addition to these, woody impurities are present to the extent of 14—17 per cent. Free cinnamic acid occurs in gum benzoïn, although to a less extent than free benzoic acid; by far the greater part of it, however, exists in combination. By hydrolysis of the mixture of benzoresinol and resinotannol cinnamates, there are obtained cinnamic acid and two alcohols—the white, crystallised *benzoresinol*, $C_{16}H_{24}O_2$, and the brown, amorphous *resinotannol*, $C_{18}H_{20}O_4$. From benzoresinol there were obtained a *potassium derivative*, and *methyl*, *ethyl*, and *isobutyl* (mono-) *derivatives*; these all crystallise in white needles. Benzoresinol itself yields, with strong nitric acid an amorphous oxidation product containing nitrogen; no acetic or benzoic derivative could be obtained from it, and no oxime; with bromine, it yields an amorphous bromo-derivative. From resinotannol were obtained a *potassium salt* and a *monethyl derivative*, both as brown, amorphous substances. Resinotannol itself is oxidised by strong nitric acid to picric acid; dilute nitric acid forms a nitro-derivative, and an oxidation product of the nature of a phlobaphen; bromine forms amorphous bromo-derivatives very rich in bromine. When reduced, it yields a white substance which oxidises so readily that it could not be further investigated. When

fused with caustic potash, it yields butyric acid, phenol, and protocatechuic acid.

The bark of uninjured trees of *Styrax Benzoïn Dryand* contains, besides traces of wax and a little phloroglucinol and sugar, large quantities of a tannin which very readily oxidises to a phlobaphen, *benzophlobaphen*, $C_{21}H_{20}O_{21}$, a lustrous, reddish-black powder.

Since the uninjured bark contains neither secreting vessels nor secretions, but, on the other hand, does contain a large quantity of tannin, particularly in the medullary rays, and since gum benzoïn contains large quantities of an alcohol, resinotannol, which has the characters of a tannin, and since, finally, the formation of resin begins in the medullary rays, therefore it is probable that the gum is formed from the tannin of the bark, increases in amount by a process of backward metamorphosis of the cell-membranes, and is then stored up in lysigenetic spaces; if these spaces increase largely in bulk, they form resin glands. C. F. B.

Constituents of Sumatra Gum Benzoïn. By E. Schmidt (*Arch. Pharm.*, **231**, 95—98).—A large quantity of genuine gum benzoïn from Sumatra was examined some time ago by C. Denner, a former demonstrator in the author's laboratory: the results were, however, never published, owing to the death of Denner, and loss of his MSS. His results confirmed, to a large extent, those of Lüdy (preceding abstract), and he was able to demonstrate more satisfactorily than the latter the existence of benzaldehyde and cinnamene in the gum. C. F. B.

Adonite. By E. Merck (*Arch. Pharm.*, **231**, 129—131).—Adonite, $C_5H_{12}O_5$, is contained to the extent of 4 per cent. in the flowering shoots of *Adonis vernalis*. It crystallises from water in long, colourless prisms, from alcohol in short, white needles, melts at 102°, and decomposes when distilled, is a neutral substance, and does not reduce Fehling's solution; possibly it is a pentahydric alcohol. It is without specific physiological action. C. F. B.

Cerberin. By P. C. Plugge (*Arch. Pharm.*, **231**, 10—34).—This substance discovered by De Vrij, occurs in the seeds of an Indian tree, *Cerbera odollam*, Gaertn. (*C. mangas*, L.; *Tanghinia odollam*, Don.). It forms colourless, odourless crystals with a bitter taste, turns yellow at 180—185°, and melts at 191—192° (corr.). It dissolves in the following substances, 1 part in the indicated number of parts of the solvent at 16—21°:—Chloroform, 8·83; alcohol, 90 per cent., 12·43, absolute, 12·89, 75 per cent., 27·27; isobutyl alcohol, 14·7; amyl alcohol, 14·87; ether, 178·5; benzene, 544·7; carbon tetrachloride, 813; water, 5555 (at 100°, 4974); carbon bisulphide, 12,487; light petroleum (sp. gr. 0·675), 36,730. It has the following values of specific rotation, $[\alpha]_D$; in 90 per cent. alcohol, −74·61°; in ether, −64·76°; in chloroform, −74·82°; in acetic acid, −80·81°. Analysis and molecular weight determinations lead to the formula $C_{27}H_{40}O_8$; but its properties show that it is not identical either with the tanghinin of Arnaud or with the thevetin of De Vrij. It exhibits

the following colour reactions:—I. Yellow coloration when warmed with dilute sulphuric, hydrochloric, or nitric acid. II. Polychroic solution (orange-yellow-violet-blue) in concentrated sulphuric acid. III. A quickening, emphasising, and sometimes a characteristic modifying, of colour reaction II, when to the sulphuric acid are added small quantities of (*a*) phenols (thymol, α-naphthol, cresol, or glycocholic acid), or (*b*) aldehydes (furfuraldehyde, cane sugar, vanillin, heliotropin, &c.). Reaction III (*a*) seems to indicate that cerberin is a glucoside, III (*b*) that it is a phenol. As a matter of fact, cerberin is hydrolysed when heated with alcoholic sulphuric acid for two hours, and yields a small quantity of sugar, probably glucose, and 62 per cent. of *cerberetin* $C_{19}H_{26}O_4$ (?), a lemon-yellow, amorphous powder, which melts at 85·5° (corr.), is optically inactive, and is precipitated from its solution in alcohol by the addition of water; the alcoholic solution has, even when diluted to 1 : 5000, a perceptible yellow colour. Like cerberin, it is a poison. Observations of the physiological action of cerberin agree with those of Zotos (Dissertation, Dorpat, 1892); it has the advantages, without the disadvantages, of digitalin. C. F. B.

Glucoside of Ipomœa pandurata (Convolvulus panduratus, L.). By N. Kromer (*Chem. Centr.*, 1893, i, 427—428; from *Pharm. Zeit. Russ.*, **32**, 1—5, 17—21, 33—38).—The drug *Ipomœa pandurata*, Meyer (man in the ground root, man root, man of the earth, wild jalap, and wild potato), is used in America as a remedy for lithiasis. The root is cylindrical, 2—3 feet in length and 1 or more inches in thickness; it diminishes in thickness suddenly to the size of a finger, and exudes a milky, resinous juice. Its exterior is greyish-brown and its interior greyish-white; it has a characteristic bitter taste.

In order to obtain the glucoside described by Manz (1881), the author employed the method used for extracting the glucosides from other *Convolvulaceæ* (*Chem. Centr.*, 1893, i, 310), and found that the chief constituent of the root was a compound *ipomœïn*, $C_{78}H_{132}O_{38}$, together with a small quantity of a semi-fluid compound. Ipomœïn is a white powder, melting at 170°, soluble in most solvents except ether, gives a red coloration with sulphuric acid and an intense red coloration with sodium hydroxide. By the action of barium hydroxide, a volatile acid, $C_5H_8O_2$ (probably β-methylcrotonic acid) is formed together with *ipomœic acid*, $C_{34}H_{62}O_{18}$, which is a bright-yellow amorphous powder; it softens at 115° and melts at 135—140°. Mineral acids convert the last-named acid into *ipomeolic acid*, a monobasic acid crystallising in concentrically grouped needles, and melting at 60·6°, and a cupric reducing sugar giving a *phenylhydrazine compound* (?) melting at 198°.

Ipomœïn is decomposed by mineral acids into ipomeolic acid, a sugar, and a volatile acid, $C_5H_8O_2$, (m. p., 60·8°), which is perhaps β-methylcrotonic acid. Nitric acid converts ipomœïn into a sebacic acid, $C_{10}H_{18}O_4$, which crystallises in needles, is soluble in hot water, and melts at 98·6°, together with a valeric acid. A. R. L.

Derivatives of Cantharidin. By F. ANDERLINI (*Gazzetta*, **23**, i, 121—128).—Cantharidin dissolved in absolute alcohol is reduced by sodium; after treating the product with water, distilling off the alcohol, and acidifying, the unchanged cantharidin is deposited and may be separated. By extracting with ether, evaporating, dissolving the residue in benzene, and fractionally precipitating by petroleum, a colourless, crystalline *substance* is finally obtained; this has the composition, $C_{10}H_{14}O_3$, melts at 129°, and is very soluble in alcohol or benzene, but less so in water.

Cantharidin hydrazone dissolves in nitric acid yielding a bright yellow *dinitro*-derivative, $C_{16}H_{16}(NO_2)_2NO_3$, which does not melt at 320°; it dissolves in glacial acetic acid, but is insoluble in most other solvents. With alkalis, it gives a scarlet colour; on reduction with zinc dust and acetic acid, a red or yellow solution is obtained, from which the substance melting at 201° previously described by the author (Abstr., 1890, 640) may be isolated. Nothing but negative results were obtained on reducing the nitrohydrazone with sodium in alcoholic solution.

On boiling cantharidinimide with phosphorus oxychloride, a *substance* of the composition $C_{10}H_{11}NO_2$ is produced; it forms monosymmetric prisms, $a:b:c = 2{\cdot}001:1:?$; $\beta = 65°\ 28'$, melting at 137°.

W. J. P.

Action of Diamines on Cantharidin. By F. ANDERLINI (*Gazzetta*, **23**, i, 128—139).—On mixing an alcoholic solution of ethylenediamine with finely divided cantharidin, heat is developed, and a white additive *compound*, $C_{10}H_{12}O_4,C_2H_4(NH_2)_2$, is formed; it melts at 195° with decomposition, is very soluble in water, but insoluble in alcohol, ether, or benzene, and gives cantharidin when boiled with hydrochloric acid. A *compound* of the composition $C_{11}H_{14}O_3N$ is obtained on heating the mixture of alcohol, ethylenediamine, and cantharidin in a closed tube at 100°; it forms colourless, flattened, monosymmetric prisms of pearly lustre, $a:b:c = 2{\cdot}2811:1:1{\cdot}7906$; $\beta = 75°\ 58'$. It melts at 219—220° and is soluble in most of the ordinary solvents. It is a neutral substance, and is not attacked by long heating with potash or baryta. After separating this compound, a *base* of the composition $C_{12}H_{18}O_3N_2$ is found in the mother liquors. It is a white crystalline substance which melts at 94—95°, when deposited from its syrupy aqueous solution; it separates from ether in transparent crystals which melt at 50—53° owing to their containing ether of crystallisation; this is lost on exposure to air. The *hydrochloride* is employed in the purification of the base; it forms colourless, transparent, anorthic plates, $a:b:c = 1{\cdot}2639:1:0{\cdot}5515$; $\alpha = 75°\ 27'$, $\beta = 78°\ 42'$, $\gamma = 90°\ 55'$; it is very soluble in water, but only sparingly so in alcohol. The *platinochloride* is obtained in brilliant-yellow prisms or laminæ and turns brown at 250°; it is soluble in water.

On heating cantharidin and orthophenylenediamine in glacial acetic acid solution in a reflux apparatus, condensation occurs with elimination of $2H_2O$ and a white, crystalline *substance* is obtained, which has the composition $C_{16}H_{16}O_2N_2$, and melts at 163°. It is neutral towards in-

dicators, and insoluble in dilute acids, but dissolves in the ordinary solvents, with the exception of water.

Orthotoluylenediamine reacts in the same way with cantharidin, yielding a crystalline *substance* of the composition $C_{17}H_{17}O_2N_2$, which melts at 180—181° and is similar in properties to the preceding compound. W. J. P.

New Method of synthesising Hydropyridine Compounds. By J. Guareschi (*Chem. Centr.*, 1893, i, 699—700; from *Ann. Chim. Farm.*, **17**, 83—87).—The method consists in the action of ethylic cyanacetate on acetone or other ketones in the presence of ammonia; or in other words, the action of ethylic cyanacetate on diacetonamine, which latter is formed during the reaction. When an ethereal solution of the ready-formed diacetonamine is treated with ethylic cyanacetate, a white compound melting at 194—195·5° is obtained; it is also formed by treating acetone or mesityl oxide, saturated with dry ammonia, with ethylic cyanacetate. The author believes this compound to be *cyanotrimethyldihydro-2-pyridone*,

$$NH\begin{<}CMe_2\cdot CH_2\\CO\cdot C(CN)\end{>}CMe.$$

Similar compounds are formed when instead of ammonia a primary amine is used. The *compound* $C_{10}H_{14}N_2O$, obtained from acetone, methylamine, and ethylic cyanacetate, melts at 142—143·5°, and is more sparingly soluble in potash than the lower homologue. On oxidation with permanganate, two crystalline compounds are obtained; one is an *amide*, and the other an acid melting at 172—174°; the latter gives a blood-red coloration with ferric chloride. The corresponding *benzyl* derivative, $C_{16}H_{18}N_2O$, melts at 168—169°; and the *allyl* derivative, $C_{12}H_{16}N_2O$, melts at 152—153·5°. A. R. L.

4′-Bromonicotinic Acid. By A. Claus and E. Pychlau (*J. pr. Chem.* [2], **47**, 414—420).—4′-Bromonicotinic acid (Abstr., 1892, 876) forms tabular or columnar, vitreous crystals, with $2H_2O$; it melts at 183°, and sublimes without decomposition. The *ammonium* salt, $C_5NH_3Br\cdot COONH_4$, the *sodium* salt with $1H_2O$, the *potassium* salt with $1\frac{1}{2}H_2O$, the *calcium* salt with $2H_2O$, the *barium* salt with $4H_2O$, the *silver* salt, the *cobalt* salt with $1H_2O$, the *nickel* salt with $2H_2O$, and the *copper* salt are described.

The acid previously described as 3′-bromonicotinic acid (*loc. cit.*), is now shown to be *nicotinic acid hydrobromide*, $C_5NH_4\cdot COOH,HBr$, and is remarkable for the constancy of its melting point (275°), and for its subliming unchanged.

4′-*Bromonicotinic acid hydrobromide* crystallises from a solution of the acid in hydrobromic acid in aggregates of needles, melts at 243°, and sublimes unchanged. A. G. B.

Hydroxyquinolines. By A. Claus and H. Howitz (*J. pr. Chem.* [2], **47**, 426—438; compare Abstr., 1892, 878).—1-*Hydroxyquinoline* 1′-*ethobromide* crystallises in hard, yellow prisms with $2\frac{1}{2}$ mols. H_2O,

and when dried at 100° melts at 166°. The "*intermediate product*," $OH{\cdot}C_9NH_6Et{\cdot}O{\cdot}C_9NH_6EtBr$, obtained by decomposing the ethobromide in aqueous solution with half a molecular proportion of an alkali hydroxide, crystallises in slender, scarlet needles, and when quickly heated, melts at 177° (compare Abstr., 1892, 878). This product is also formed when an excess of alkali is used if the solution be dilute and cold, otherwise 1-*hydroxyquinoline*-1′-*ethoxide* is produced; this crystallises in large, brilliant, dark-red tables or columns with $1H_2O$, and dissolves easily in alcohol, but not at all in absolute ether; it melts in its water of crystallisation at 72°, and, when anhydrous, softens at 220°, but decomposes before fusion.

The 1′-*benzochloride*, $OH{\cdot}C_9NH_6Cl{\cdot}CH_2Ph$, is prepared by heating its components at 130—135° in a sealed tube for 18—20 hours; it forms small, golden-coloured crystals with $1H_2O$, melts in its water of crystallisation at 75°, and when anhydrous at 182°, and dissolves in hot water. The "*intermediate product*,"

$$OH{\cdot}C_9NH_6(CH_2Ph){\cdot}O{\cdot}C_9NH_6Cl{\cdot}CH_2Ph,$$

crystallises in slender, orange-red needles with $1H_2O$, melts with decomposition at about 145°, and dissolves easily in water. The *benzohydroxide* crystallises in large, brilliant, dark-red prisms and columns with $1H_2O$; it melts in its water of crystallisation at 66°, and when anhydrous between 140° and 150°; it dissolves in water, but not in ether.

It has been previously stated (*loc. cit.*) that a quaternary ammonium hydroxide, sufficiently stable not to become converted into a base soluble in ether, is only produced from a hydroxyquinoline alkyl haloïd when the hydroxyl group has the 2- or 3-position in the benzene ring. The obtaining such compounds from 1-hydroxyquinoline derivatives, as described above, refutes the statement in question, which must therefore be withdrawn.

4-*Hydroxyquinoline* has been obtained by the usual reactions from quinoline-4-sulphonic acid, and from 4-amidoquinoline; it is a pale-yellow, crystalline powder, which melts with decomposition at 224°. The *hydrochloride* forms small, yellow crystals, and melts at 240°. The *platinochloride*, with $4H_2O$, is described. The *methiodide* crystallises both in short, brownish-red, lustrous columns, and in thin, golden-yellow aggregates of ill-defined form; both melt at 224°, and dissolve somewhat easily in water, separating therefrom as a viscid oil, which slowly solidifies. The *methohydroxide* crystallises in brilliant, dark-red, vitreous columns, and dissolves in water and alcohol, but not in ether.

A recantation is also necessary with regard to the action of potassium hydroxide on 4-hydroxy-3-chloroquinoline methiodide (*loc. cit.*). The authors have since found that their ether contained alcohol, which dissolved the base produced, and that when pure ether is used nothing is dissolved, so that in this case also the methoxide formed is insoluble in ether.

Further investigations are being conducted on the bases derived from the alkyl haloïds derived from the hydroxyisoquinolines (compare *loc. cit.*). A. G. B.

Pyrazines and Piperazines. By C. Stoehr (*J. pr. Chem.* [2], **47**, 439—522).—The author has prepared pyrazine by distilling piperazine, or its hydrochloride, with zinc-dust, the yield being about 10 per cent. Obtained in this way, it is a limpid, mobile, highly refractive liquid, which boils at 138—140° (corr.); it volatilises easily with steam, and has a penetrating odour resembling that of the pyridine bases; it dissolves easily in water, alcohol, and ether, and is separated from its aqueous solution by caustic alkalis; its sp. gr. at 0°/4° is 1·0317; it is a feebler base than its homologues, and has not yet been crystallised (compare Wolff, this vol., i, 373). The hydrochloride is easily dissociated. The picrate forms yellow needles. The *mercury chloride* compound, $C_4H_4N_2,HgCl_2$, is very sparingly soluble, and forms lustrous crystals. The aurochloride, $C_4H_4N_2,HAuCl_4$, crystallises in lustrous, yellow laminæ, and melts with decomposition at 245° (compare Wolff, *loc. cit.*).

2 : 5-*Dimethylpyrazine*, $N\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{\cdot}CH\\CH{:}CMe\end{matrix}\begin{matrix}>\\<\end{matrix}N$, has been already described as dimethyldiazine (Abstr., 1891, 581; 1892, 507). Besides the platinochlorides previously described (Abstr., 1891, 581), the *salt* $(C_6H_8N_2)_2,H_2PtCl_6 + 4H_2O$ has been obtained. The aurochloride crystallises with $1H_2O$, not $\frac{1}{2}$ mol., as previously stated (*loc. cit.*), and, when anhydrous, melts at 153°. The *mercury chloride* compounds, $C_6H_8N_2,2HgCl_2$, and $C_6H_8N_2,3HgCl_2$, are described, and a third one, containing even more mercuric chloride, was crystallised, but not analysed. The solutions of the base are also precipitated by zinc chloride and silver nitrate. The *picrate*, $C_6H_8N_2,C_6H_2(NO_2)_3{\cdot}OH$, crystallises in laminæ, prisms, and needles, and melts at 157° (compare Abstr., 1892, 507).

Ketine, another dimethylpyrazine, was studied by Treadwell and Steiger (Abstr., 1882, 941). It is best prepared by reducing isonitrosoacetone with zinc and hydrochloric or acetic acid. It is a colourless, highly refractive liquid, which boils without decomposition at 155° (760 mm., mercury column in vapour), and resembles 2 : 5-dimethylpyrazine in odour; indeed there is reason to believe that these two bases are identical. Ketine dissolves in water with alkaline reaction, and separates again on the addition of caustic alkali. Its sp. gr. at 18°/4° is 0·9896; when quickly cooled, it crystallises in rhombohedra, which melt above 15°. The platinochlorides are quite similar to those of 2 : 5-dimethylpyrazine (see above), and the resemblance obtains with all the other salts which are described.

2 : 5-*Dimethyl*-3-*ethylpyrazine*, $N\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{\cdot}CEt\\CH{:}CMe\end{matrix}\begin{matrix}>\\<\end{matrix}N$, has been already described (Abstr., 1891, 582). Its constitution is settled by the fact that its oxidation product, $C_7H_8N_2O_2$, yields 2 : 5-dimethylpyrazine by loss of carbonic anhydride. The *platinochlorides*, $C_8H_{12}N_2,H_2PtCl_6 + 2H_2O$; $C_8H_{12}N_2,HCl,PtCl_4$; and $C_8H_{12}N_2,PtCl_4$, are described. The *mercurochloride*, *argentonitrate*, and *zincochloride* were obtained. The *picrate* crystallises in long, yellow needles, and melts at 142°. The *methiodide* crystallises in laminæ and needles, and melts with decomposition at 236—237°

Pyrazinecarboxylic acid, the ultimate product of the oxidation of dimethylethylpyrazine with potassium permanganate, crystallises in needles (with $1\frac{1}{2}$ mols. H_2O), melts, with decomposition, at 177°, and partially sublimes; it dissolves in hot water, alcohol, ether, hot benzene, and hot chloroform; with ferrous chloride, it gives a violet-red colour. A *platinochloride* can be obtained in a strong hydrochloric acid solution of the acid. The *ammonium*, *barium*, *calcium*, *tin*, *lead*, *silver*, *copper*, *cobalt*, *nickel*, and *mercury* salts were prepared.

2-Methylpyrazine-5-carboxylic acid is obtained by oxidising 2 : 5-dimethylpyrazine with sufficient potassium permanganate to oxidise only one of the methyl groups; it forms lustrous laminæ and prisms (measurements given), melts with decomposition at 200°, and dissolves in hot water, alcohol, and hot benzene. It sublimes very readily, and gives a yellow colour with ferrous sulphate. Its salts are for the most part soluble, the most characteristic being the *silver salt*, which crystallises in long, slender needles.

2 : 5-*Dimethylpyrazine-3-carboxylic acid* is the first product of oxidation of dimethylethylpyrazine, and is prepared by limiting the quantity of potassium permanganate to that necessary to oxidise the ethyl group. It crystallises in prismatic needles with $1H_2O$, melts, when anhydrous, at 117°, and sublimes undecomposed. It dissolves in hot water, alcohol, ether, chloroform, and benzene, and gives a yellow colour with ferrous sulphate. A *platinochloride* was crystallised, and the *ammonium*, *calcium*, *barium*, *tin*, *lead*, and *mercury* salts were prepared, and found to be soluble in water; the *cobalt*, *nickel*, and *copper* (with $4H_2O$) salts are only sparingly soluble; the *silver salt* is very sparingly soluble. The constitution of the acid is settled by the production of 2 : 5-dimethylpyrazine when it is heated with glacial acetic acid at 180—200° in a sealed tube.

2 : 5-*Pyrazinedicarboxylic acid* has been already described as diazinedicarboxylic acid (Abstr., 1892, 507).

Pyrazinetricarboxylic acid is obtained in small quantity during the oxidation of dimethylethylpyrazine; it crystallises in colourless needles with $1H_2O$, and becomes red on exposure to air. It melts at 250—251° with decomposition.

α-2 : 5-Dimethylpiperazine, $NH<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHMe\end{matrix}>NH$, is obtained by the action of sodium in alcohol on dimethylpyrazine. It crystallises in prisms and tables, melts at 118°, and dissolves in water and alcohol, but not in ether. It is very volatile, and boils at 162° (mercury column in vapour, 746·5 mm.). An aqueous solution of the base, like ammonia, precipitates many metallic oxides. The *hydrochloride*, $C_6H_{14}N_2,2HCl$, forms prismatic crystals, and is very soluble in water; it sublimes unchanged when sharply heated. The *hydrobromide* is also described; the crystallography of both salts is given. The *sulphate*, $C_6H_{14}N_2,H_2SO_4 + H_2O$, crystallises in lustrous prisms very soluble in water. The *dichromate*, $C_6H_{14}N_2,H_2Cr_2O_7$, the *phosphates*, $3C_6H_{14}N_2,2H_3PO_4$, and $C_6H_{14}N_2,2H_3PO_4$, and the *tartrate*, $C_6H_{14}N_2,C_4H_6O_6 + 3H_2O$ (m. p. of anhydrous salt 242—243°) all

crystallise well, and are crystallographically described. The *platinochloride*, $C_6H_{14}N_2,H_2PtCl_6$, crystallises both in an anhydrous form and with 2 or with 3 mols. of water. The *aurochloride*, $C_6H_{14}N_2,2HAuCl_4$, is sparingly soluble. The *mercury chloride*, $C_6H_{14}N_2,2HCl,4HgCl_2$, crystallises in lustrous, prismatic needles, and melts with decomposition at 235—236°; its crystallography is detailed. The *picrate*, $C_6H_{14}N_2,2C_6H_3N_3O_7$, forms sparingly soluble, yellow needles. The *bismuthoiodide* is a red, crystalline powder, soluble in water. The *dinitrosamine*, $C_6H_{12}N_2(NO)_2$, obtained by the action of sodium nitrite on the hydrochloride in hydrochloric acid, crystallises in prisms or needles, melts at 172°, and dissolves in water, alcohol, chloroform, and, less easily, in water. The *dibenzoyl* derivative, $C_6N_2H_{12}Bz_2$, obtained by shaking the aqueous solution of the hydrochloride with sodium hydroxide and benzoic chloride, crystallises from alcohol in lustrous rhombohedra, and melts at 225°; the crystallography is detailed.

The 2 : 5-dimethylpiperazine prepared from ketine appears to be identical with that just described.

Dimethylpiperazyldihydrazine, $NH_2{\cdot}N<\begin{matrix}CH_2{\cdot}CHMe\\CHMe{\cdot}CH_2\end{matrix}>N{\cdot}NH_2$, is obtained by reducing the above-described dinitrosamine with zinc-dust and acetic acid, and distilling with alkali; it crystallises in lustrous, stellate prisms with $6H_2O$; it sublimes readily in the form of prisms which melt at 110—111°, and dissolves easily in water, but less freely in other solvents. The *hydrochloride* forms rhombohedral, or hexahedral crystals, melts with decomposition at 225°, and is sparingly soluble in alcohol and water. The *picrate* is sparingly soluble, and forms small, yellow needles.

β-Dimethylpiperazine occurs together with α-2 : 5-dimethylpiperazine, from which it is separated by the greater solubility of its *hydrochloride* in absolute alcohol. The free base crystallises in dazzling, white laminæ, and boils at 161—162°. The *platinochloride* does not crystallise with water. The *aurochloride* crystallises with $3H_2O$, the measurements of the crystals being given. The *mercury chloride* is $C_6H_{14}N_2,2HCl,5HgCl_2$. The *dinitrosamine* crystallises in large, thin laminæ, melts at 95—96°, and is sparingly soluble in water, but much more soluble in alcohol than the dinitrosamine of the α-base. The *dibenzoyl* derivative is also more soluble in alcohol than is that of the α-base; it crystallises in lustrous tables, and melts at 151—152°. The author discusses the possible difference in structure between these two bases.

2 : 5-*Dimethyl*-3-*ethylpiperazine*, $HN<\begin{matrix}CHMe{\cdot}CHEt\\CH_2—CHMe\end{matrix}>NH$, prepared by reducing the corresponding pyrazine with sodium in alcohol, crystallises (with water) in lustrous prisms; it melts in its water of crystallisation at 62°, and boils at 173—174°, but the melting and boiling points of the anhydrous base have not been ascertained; it dissolves in water and benzene, but not in ether. The *hydrochloride*, $C_8H_{18}N_2,2HCl$, is easily soluble in water, but sparingly in alcohol; it sublimes easily. The *platinochloride*, $C_8H_{18}N_2,H_2PtCl_6 + 3H_2O$, is described, and crystallographical measurements of it are given. The

picrate crystallises in yellow needles or lamiuæ. The *dinitrosamine* crystallises in flat needles, and melts at 92°. A. G. B.

Constitution of Nicotine. By F. Blau (*Ber.*, **26**, 1029—1034).—After replying to Pinner's criticism (this vol., i, 443) of his previous paper, the author points out that on the reduction of nicotine by Liebrecht's method, a mixture of hexahydronicotine and octohydronicotine is obtained; the latter is a diimide base, and on treating the hydrochloride with nitric acid, it yields *dinitroso-octohydronicotine*, $C_{10}H_{20}N_2(NO)_2$; the corresponding dibenzenesulphonic derivative, $C_{10}H_{20}N_2(SO_2Ph)_2$, is crystalline, and melts at 143·5°; it appears to be identical with the corresponding compound (m. p. 133—134°) stated by Pinner to be derived from hexahydronicotine.

Hexahydronicotine is separated from the octohydrogenated base by fractional precipitation of the platinochlorides, of which the latter is the more soluble, and contains a secondary and a tertiary nitrogen atom; it boils at 244·5—245·5° (corr.), crystallises when anhydrous, and melts at about blood heat. The *hydrochloride* is hygroscopic; the *platinochloride* melts at 226—228° with decomposition; the *aurochloride* darkens at 175°, and decomposes at 190—191°; the *picrate* is crystalline. The *nitroso-derivative*, $C_{10}H_{19}N_2{\cdot}NO$, is soluble, and yields a *platinochloride* which decomposes at 150—152°, and a crystalline *picrate* melting at 140°. In the purification of hexahydronicotine, a base is obtained which has the formula $C_{11}H_{22}N_2$, and boils at 243—245°; its *platinochloride* resembles that of hexahydronicotine in properties and appearance. J. B. T.

Salts of Caffeïne. By E. Schmidt (*Arch. Pharm.*, **231**, 1—10).—Since the existence of salts of caffeïne has recently been called in question by Tanret, the matter has been again investigated, and the following salts prepared. Their preparation is a little difficult, as they are readily decomposed by water. The *nitrate*, $C_8H_{10}N_4O_2,HNO_3$, forms large, colourless tables: the *sulphate*, $C_8H_{10}N_4O_2,H_2SO_4$, rosette-shaped groups of white needles which, on exposure to the air, take up $1H_2O$; the *acetate*, $C_8H_{10}N_4O_2,2C_2H_4O_2$; the *propionate*,

$$C_8H_{10}N_4O_2,2C_3H_6O_2;$$

the *citrate*, $C_8H_{10}N_4O_2,C_6H_8O_7$, forms cauliflower-like groups of crystals; the *formate*, *butyrate*, *isobutyrate*, and *isovalerate* could not be obtained pure. C. F. B.

Papaverine Ethobromide. By A. Claus (*J. pr. Chem.* [2], **47**, 523—531).—The author has reinvestigated the crystallography of papaverine ethobromide (Beckenkamp, *Zeit. Kryst. Min.*, **12**, 161; Foullon, *Monatsh.*, 1889, **10**, 684), and finds that the observed difference in crystalline form between different batches does not depend on whether the ethobromide has been made from purified or unpurified papaverine.

Two bases are obtainable by treating the ethobromide with alkalis; the one is colourless, and soluble in water, but not in ether; the other is yellow, and soluble in ether; the action of silver oxide yields the

former. The decomposition occurs in the cold, in which respect papaverine alkyl haloïds differ from those of narceïne and the cinchona alkaloïds. The resemblance between papaverine and isoquinoline in the same connection must be noted. A. G. B.

Alkaloïds of the Papaveraceæ. By E. SCHMIDT, G. KOENIG, and W. TIETZ (*Arch. Pharm.*, **231**, 136—183).—In the introduction to the paper, a list is given of the alkaloïds known to occur in plants of this order, and the physiological properties of these alkaloïds are described. There follows, then, a detailed account of the

Alkaloïds of the root of Sanguinaria canadensis, for the method of separating which reference must be made to the original paper.

Chelerythrine, $C_{19}H_{11}(OMe)_2NO_2$, is the main constituent. It forms small, colourless, rhombohedral crystals of the formula $C_{19}H_{11}(OMe)_2$ + EtOH, often united in crusts, melts at 203°, has a blue fluorescence, and yields yellow salts. The *hydrochloride*, $C_{21}H_{17}NO_4$,HCl (+ $5H_2O$ from water, + $4H_2O$ from alcohol), *hydriodide*, and *platinochloride* form yellow needles, the *aurochloride* brown needles.

Sanguinarine, $OMe{\cdot}C_{19}H_{12}NO_3 + H_2O$, forms bundles of white needles or nodular aggregates, melts at 213°, has a bluish-violet fluorescence, and yields blood-red salts. The *hydrochloride*, $C_{20}H_{15}NO_4$,HCl (from water, $5H_2O$?; from alcohol, $2H_2O$?), and *nitrate* with $1H_2O$, form red needles, the *platinochloride* a yellow, and the *aurochloride* a reddish-brown, amorphous powder.

γ-Homochelidonine, $C_{19}H_{15}(OMe)_2NO_3$, crystallises from ethylic acetate (+ $\frac{1}{2}CH_3{\cdot}COOEt$) in large, colourless plates, melts at 169° when quite dry, when air-dried at 159—160°, and yields colourless salts. The *platinochloride* forms a yellow, the *aurochloride* a yellowish-red powder. The alkaloïd is apparently a tertiary base, for it yields a *methiodide*, $C_{21}H_{21}NO_5$,MeI, which, with moist silver oxide, yields a hydroxide, from which a *platinochloride*, $(C_{21}H_{21}NO_5)_2,Me_2PtCl_6$, was obtained as a yellow, amorphous powder.

β-Homochelidonine, $C_{21}H_{21}NO_5$, forms bundles of lustrous needles, melts at 159°, and yields colourless salts.

Sanguinaria-protopine, $C_{20}H_{17}NO_5$, crystallises in two interconvertible forms—in white, nodular aggregates and colourless, lustrous, monoclinic prisms; it melts at 207°, and forms colourless salts. The *platinochloride*, with $4H_2O$, is yellow, the *aurochloride* a reddish-brown, amorphous powder.

The protopine of the root of Chelidonium majus (*Chelidonium-protopine*) has been again prepared; it melts at 204°, and it and its platinochloride and aurochloride (melting at 198°) seem to be identical with the compounds obtained from *Sanguinaria protopine*.

The chelerythrine of the root of Chelidonium majus has been again prepared, and seems identical with the alkaloïd obtained from *Sanguinaria canadensis*. Both these alkaloïds melt at 203°, and their aurochlorides, melting at 233°, and platinochlorides are identical.

C. F. B.

Crystallised Veratrine. By E. MERCK (*Arch. Pharm.*, **231**, 135). Merck's "Veratrine cryst." is identical with the "cevadine" of other authors. It forms white crystals of the composition $C_{32}H_{49}NO_9$ +

xH_2O, melts when anhydrous at 202°, and yields a crystallised aurochloride, platinochloride, and picrate. C. F. B.

The Relation between Atropine, Apoatropine, and Belladonnine. By E. Merck (*Arch. Pharm.*, **231**, 110—115).—A further proof of the identity of Hesse's atropamine (Abstr., 1891, 228, 748; 1892, 1428) with apoatropine is given; the latter, when evaporated with fairly concentrated hydrochloric acid, is converted, like atropamine, into a substance which yields a platinochloride and an aurochloride identical with those of the belladonnine contained in the mother liquor that is obtained in the preparation of atropine. Apoatropine, which is formed from atropine by loss of water, is thus converted by dilute acids into belladonnine. C. F. B.

Hyoscyamine. By E. Merck (*Arch. Pharm.*, **231**, 115—117).—Hyoscyamine, $[\alpha]_D = -20{\cdot}25°$, when heated for a few hours with water in an open vessel at 100°, yields, besides atropine and unaltered hyoscyamine, inactive tropine and crystallised lævorotatory tropic acid ($[\alpha]_D = -7{\cdot}5°$ and $-15°$ in two separate preparations); Ladenburg and Hundt (Abstr., 1890, 74) describe this acid as an amorphous, yellow powder with $[\alpha]_D = -65{\cdot}15°$.

Hyoscyamine and hyoscine hydrobromides dissolve respectively in 0·34 and 4 parts of water at 15°, and in 2·2 and 21·5 parts of alcohol (sp. gr. = 0·820). C. F. B.

Pseudohyoscyamine. By E. Merck (*Arch. Pharm.*, **231**, 117—123).—This new alkaloïd occurs in *Duboisia myoporoïdes*, together with hyoscyamine and hyoscine. It forms small, yellowish needles of the composition $C_{17}H_{23}NO_3$, melts at 133—134°, and has specific rotation $[\alpha]_D = -21{\cdot}15°$; the *platinochloride*, with $2H_2O$, forms feather-like groups of needles which (when anhydrous ?) begin to melt at 116° and decompose below 150°; the *aurochloride* forms thin, yellow, lustrous plates melting at 176°; the *picrate* forms yellow needles melting at 220°. (The following *picrates* were prepared for purposes of comparison: from atropine, yellow plates melting at 175—176°; hyoscyamine, crusts of needles or quadrangular plates, melting at 161—163°; hyoscine, slender matted needles melting at 160—162°.) Pseudohyoscyamine, when hydrolysed by boiling with barium hydroxide in dilute alcohol, yields tropic acid and a base isomeric with atropine; the *platinochloride*, $2C_9H_{15}NO,H_2PtCl_6 + H_2O$, of this base forms reddish-yellow, crystalline masses which become discoloured at 210°, and get gradually blacker as the temperature rises. C. F. B.

Hydrastine Hydrogen Tartrate. By E. Merck (*Arch. Pharm.*, **231**, 134—135).—*Hydrastine hydrogen tartrate*,

$$C_{21}H_{21}NO_6,C_4H_4O_6 + 4H_2O,$$

is the first simple salt of this base which has been obtained crystallised. It forms white needles, and can be advantageously utilised for the purification of hydrastine. C. F. B.

Alkaloïds from Corydalis cava. By E. MERCK (*Arch. Pharm.*, **231**, 131—134).—The following alkaloïds occur in the roots of this plant; they are arranged in descending order of relative amount: (1) *Bulbocapnine*, melting at 199°; (2) *Corydine*, an amorphous substance which produces violent epilepsy, terminating fatally when administered hypodermically to a cat; (3) *Corydaline*, melting at 135°; (4) a base (? *Corycavine*), which crystallises in small, matted needles and melts at 218°. The first two are more pronouncedly basic than the last two (compare Dobbie and Lauder, Trans., 1892, 244, 605; 1893, 485). C. F. B.

Gelseminine. By L. SPIEGEL (*Ber.*, **26**, 1054—1060).—Pure gelseminine from *Gelsemium sempervirens*, is amorphous, softens at 105°, and melts at about 120° with partial decomposition; it is precipitated from its salts by ammonia, alkalis, and alkali carbonates, and is soluble in excess of these reagents; it is not altered by fusion with potassium hydroxide. The *hydrochloride* crystallises in concentric prisms which darken at 330° without melting; the *hydrobromide* and *hydriodide* are crystalline and unstable; the *sulphate* is amorphous; the *nitrate* is deposited from alcohol in strongly refractive octahedra or tetrahedra, and melts at 188° with decomposition. The *platinochloride* is yellow and probably amorphous; the *aurochloride* is also amorphous and brown in colour.

Gelseminine does not contain any methoxy-groups, as is shown by its behaviour towards hydriodic acid; with phenylhydrazine, a crystalline compound is formed in small quantity, but has not been investigated.

Gelseminine methiodide crystallises with $2H_2O$ and melts at 285° with decomposition; it does not react with alkalis but is decomposed by silver oxide yielding an amorphous substance. On fusion with potash, the methiodide is resolved into two nitrogenous bases, one of which is volatile, has a fishy smell, and yields a crystalline *hydrochloride*.

Gelseminine yields two products on oxidation with potassium permanganate; the one is yellowish-brown and amorphous, the other is a colourless acid; both are being further investigated. With dilute nitric acid, the base yields a number of brown indefinite products together with an acid, $C_{17}H_{20}N_2O_8$, which is deposited from alcohol in pale yellow crystals; it darkens at 350° without melting, and is not acted on by concentrated nitric acid. The brown compounds, on treatment with concentrated nitric acid, yield a colourless, crystalline substance.

Gelseminine combines with one equivalent of acids; the author has made numerous analyses of the base, the hydrochloride, and the nitrate; his results show that Sonnenschein's formula, $C_{22}H_{30}N_2O_4$, is incorrect, but they are inadequate to distinguish between the formulæ $C_{24}H_{28}N_2O_4$ and $C_{22}H_{26}N_2O_3$. The identity or otherwise of gelseminine and gelsemine is also undetermined. J. B. T.

Organic Chemistry.

Recognition of Paraffin and of Lubricating Oil in the Distillate of Train Oil under Pressure. By C. Engler and L. Singer (*Ber.*, **26**, 1449—1451).—The higher-boiling portions of the distillate were extracted with sodium hydroxide solution to remove any undecomposed fatty compounds, and allowed to remain in a freezing mixture for a week, when a solid, crystalline paraffin separated; when dissolved in light petroleum, and the solution poured into 75 per cent. alcohol, it was obtained as a white, crystalline mass; it melted at 49—51°.

To isolate the lubricating oil, the crude distillate was shaken successively with sodium hydroxide solution, water, sulphuric acid, and then again with water; after fractional distillation, the fractions were shaken successively with concentrated sodium hydroxide solution, water, sulphuric acid, water, sodium hydroxide and water, and again distilled. The heavy oil was of a yellowish-brown colour, and exhibited a strong fluorescence after washing with sodium hydroxide solution. The specific viscosity of the fraction boiling at 290—300° was 1·6 at a temperature of 50—60°, water being taken as unity, and that of a fraction boiling above 300° was 3·4. The constitution of these high-boiling oils could not be determined, and it was not, therefore ascertained whether they were identical with the synthetic products of Krämer and Spilker (Abstr., 1891, 1462).

A. R. L.

Licarene from Licareol. By P. Barbier (*Compt. rend.*, **116**, 993—994).—When licareol (Abstr., 1892, 1236, and this vol., i, 495, 496) is heated with acetic anhydride at 150°, it yields *licarene*, $C_{10}H_{16}$, a very mobile liquid with an agreeable odour. This boils at 176—178° under ordinary pressure; sp. gr. at 0° = 0·8445; index of refraction for λ 645 = 1·4741, and for λ 452·6 = 1·4922, at 17°. At 20·2° its rotatory power $[\alpha]_D = +7° 51'$, and is, therefore, opposite in sign to that of licareol. Licarene combines with bromine to form a mixture of a liquid and a solid tetrabromide, the latter melting at 103—104°. When treated with chromic mixture, it yields terpenylic acid and acetic acid. When treated with dry hydrogen chloride in acetic acid solution, it yields an inactive *dihydrochloride* boiling at about 155° under a pressure of 39 m.; sp. gr. at 0° = 1·0446; index of refraction for λ 645 = 1·4819, and for λ 452·6 = 1·4948. The same dihydrochloride is obtained by the direct action of hydrogen chloride on licareol.

Licarene yields a crystalline nitrosochloride, $C_{10}H_{16}NOCl$, and this, when boiled with alcoholic potash, yields nitrosolimonene or carvoxime. It would seem from this and the other properties that licarene belongs to the limonenes of Wallach. The latter form crystalline dihydrochlorides, but licarene dihydrochloride is probably a stereoisomeride.

C. H. B.

Constitution of Dicyanodiamide. By E. Bamberger and L. Seeberger (*Ber.*, **26**, 1583—1587).—Between the constitutional formulæ proposed by Baumann and by Bamberger for dicyanodiamide, namely, $NH{:}C{<}^{NH}_{NH}{>}C{:}NH$ and $NH{:}C(NH_2){\cdot}NH{\cdot}CN$, the experimental data have been hitherto insufficient to decide. The authors have now found that if dicyanodiamide is subjected to the continued action of zinc and dilute hydrochloric acid at the ordinary temperature, it is converted into guanidine and methylamine, the latter being probably formed by the reduction of the hydrogen cyanide first produced. To obtain direct evidence of the formation of the latter, dicyanodiamide was boiled with hydroxylamine in aqueous solution; carbonic anhydride and nitrous oxide were evolved, and the product was found to consist chiefly of a little ammeline and large quantities of guanylcarbamide. If the solution remaining after the evolution of gas has ceased was acidified with sulphuric acid and warmed, hydrogen cyanide was evolved.

The direct formation of guanidine and hydrocyanic acid shows that Bamberger's formula is correct, and that dicyanodiamide is in reality cyanoguanidine; its formation from cyanamide is, therefore, similar to that of aldol from acetaldehyde and to the polymerisation of methylic cyanide.

To detect dicyanodiamide, the best method is to boil with dilute acetic acid, which, like other acids, converts it into guanylcarbamide; the solution is then treated with soda and a small quantity of copper sulphate solution, when, if dicyanodiamide is present, pink crystals of copper guanylcarbamide separate, or if the quantity is small the biuret coloration is produced; the absence of biguanide, biuret, and guanylcarbamide from the original substance must first be ascertained.

H. G. C.

Structure of Fulminates. Dibromonitracetonitrile. By A. F. Holleman (*Ber.*, **26**, 1403—1408).—The author first gives reasons for preferring his own formula, $Hg{<}^{C{:}N{\cdot}O}_{C{:}N{\cdot}O}$, for mercury fulminate to that of Steiner, $^{C{:}NO}_{C{:}NO}{>}Hg$, recently advocated by Scholl (Abstr., 1891, 283), and then proceeds to describe a new product which he has obtained from dibromonitracetonitrile.

When dibromonitracetonitrile is heated with aniline in the water-bath, there is obtained a small quantity of a substance which crystallises in square plates melting with decomposition at 215°, and yields a *diacetyl* derivative melting, with decomposition, at a little above 200°, and a *dibenzoyl* derivative which begins to melt, with decomposition, at about 120°. This substance must be *oxanilide dioxime*, for, when heated with hydrochloric acid at 130°, it yields oxanilide and hydroxylamine, together with the decomposition products of the former, oxalic acid, and aniline. Dibromonitracetonitrile thus yields oxanilide dioxime, and must, consequently, be regarded as dibromoglyoxime peroxide. A further consequence is that mercury fulminate, from

which dibromonitracetonitrile may be obtained, must have the constitution assigned by the author,

$Br\cdot C{:}N\cdot O$ / $Br\cdot C{:}N\cdot O$	$NHPh\cdot C{:}N\cdot OH$ / $NHPh\cdot C{:}N\cdot OH$
Dibromoglyoxime peroxide ("Dibromonitracetonitrile").	Oxanilide dioxime.

C. F. B.

Ethereal Hydrogen Sulphates from Secondary Alcohols. By T. R. Krüger (*Ber.*, **26**, 1203—1204).—*Ethylpropylcarbinylic hydrogen sulphate*, $CHEtPr^{\alpha}\cdot OSO_3H$, is prepared by mixing ethylpropylcarbinol, prepared from the corresponding ketone, with sulphuric acid: the mixture is cooled for some hours, then heated to 40—50°, and diluted with water; from this solution the *barium salt*, $(C_6H_{13}SO_4)_2Ba$, is obtained in the ordinary manner; it is somewhat unstable, readily soluble in water or alcohol, and crystallises from the latter in colourless needles. The salt is not precipitated from its aqueous solution by the addition of ether, chloroform, or light petroleum.

The *strychnine salt* crystallises in monoclinic or rhombic plates; the *morphine salt* is unstable.

The constitution of the salts is shown by the fact that barium sulphate is formed on heating the strychnine salt with hydrochloric acid and barium chloride, or the barium salt with hydrochloric acid alone.

The statement that secondary alcohols do not form ethereal hydrogen sulphates thus requires modification. Bonis has previously prepared a compound of this class from methylhexylcarbinol, but the alcohol had been obtained from castor oil and may have been impure.

J. B. T.

Derivatives of Licareol. By P. Barbier (*Compt. rend.*, **116**, 883—884).—Licareol (Abstr., 1892, 1236) in a well cooled acetic acid solution combines directly with bromine, yielding an almost colourless, viscous tetrabromide, and the latter, when treated with silver hydroxide, yields a product in which the bromine has been displaced by hydroxyl.

When large quantities of licareol are oxidised, a compound of the composition $C_{10}H_{16}O$ is obtained. It is a colourless, slightly viscous liquid with an agreeable odour of citron. It boils at 118—120° under a pressure of 20 mm. and at about 224—226°, with decomposition, under the ordinary pressure; sp. gr. at 0° = 0·9119; index of refraction for λ 645 = 1·4736, and for λ 452·6 = 1·4907 at 17·8°. This compound, *licaraldehyde*, has no action on polarised light; it forms a crystalline compound with sodium hydrogen sulphite, reduces energetically an ammoniacal solution of silver nitrate, and, when treated with sodium hypobromite in presence of potassium iodide, yields no iodoform. With hydroxylamine, it yields an oily oxime, $C_{10}H_{17}NO$, which has an aromatic odour, and boils at about 150° under a pressure of 15 m.m., with slight decomposition. If this oxime is boiled for some time with acetic anhydride, it yields *licaronitrile*, $C_{10}H_{15}N$, a colourless liquid with an aromatic odour, which boils at 137—138°

under a pressure of 15 mm. When the nitrile is boiled with concentrated alcoholic potash, *licaric acid*, $C_{10}H_{16}O_2$, is obtained. This acid is also obtained in smaller quantity by the oxidation of licareol by potassium permanganate in neutral solution. It is an oily liquid, with a strong and disagreeable odour; it is only slightly soluble in water, but dissolves in ether. The barium salt is gummy; the silver salt is white and only slightly soluble in water.

When oxidised by chromic mixture, licareol yields, in addition to licaraldehyde, formic and acetic acids and a trace of butyric acid.

It would follow, therefore, that licareol is a primary alcohol which can be represented by the formula $C_9H_{15}\cdot CH_2\cdot OH$, the residue, C_9H_{15}, containing two ethylenic bonds, and being an open-chain hydrocarbon. C. H. B.

Constitution of Licareol. By P. Barbier (*Compt. rend.*, **116**, 1062—1064; compare preceding abstract).—The conversion of licareol into an active limonene, licarene, and the formation from it of carvoxime melting at 72°, indicates the presence of the groups ·CH:CH·. The relation between carvoxime, carvol, and carvacrol indicates the existence of the groups $CHMe_2\cdot$ and Me·, and hence it would follow that licareol has the constitution

(1) $CH_2{:}CMe\cdot CH{:}CH\cdot CH(CHMe_2)\cdot CH_2\cdot OH$,

or (2) $CH_2{:}C(CHMe_2)\cdot CH{:}CH\cdot CHMe\cdot CH_2\cdot OH$. A compound with the first constitution should yield valeric acid on oxidation, but licareol and licaraldehyde yield formic and acetic acids and a small quantity of isobutyric acid, but no valeric acid. It would seem, therefore, that the second formula is probably correct, and the constitution of licarene (this vol., i, 493) will be $CPr^{\beta}\!<\!\begin{matrix}CH\cdot CH_2\\CH{:}CH\end{matrix}\!>\!CHMe$. C. H. B.

Trehalum, a new Carbohydrate. By C. Scheibler and H. Mittelmeier (*Ber.*, **26**, 1331—1336).—When the residue obtained in the preparation of trehalose from trehala manna is extracted with boiling water and filtered, a crystalline precipitate of a new carbohydrate separates out in the course of 24 hours; it may be purified by washing with cold, and recrystallising from hot, water, and then forms a fine, lustrous, white, very hygroscopic powder, consisting of microscopic prisms. It appears to have the composition $C_{24}H_{42}O_{21}$, is tasteless and odourless, scarcely soluble in cold, more readily in hot, water, and, on cooling, forms supersaturated solutions. It is dextrorotatory, $[\alpha]_D = +179°$. It only reduces Fehling's solution after boiling with acids, and yields *d*-glucose as the sole recognisable product of hydrolysis.

Trehalum does not melt at 240°, but becomes slightly yellow when heated for two hours at 180°, and the product is then readily soluble in water; on addition of alcohol to the solution, a precipitate is thrown down, which may be obtained crystalline by dissolving in water and allowing the solution to remain. The product, unlike the original substance, dissolves in phenylhydrazine, and is therefore an aldehyde. The two compounds thus behave in an analogous manner

to starch and dextrin, and the authors, therefore, propose to term them *trehalum* and *trehalin*.

When iodine is added to a mixture of trehalum and water, the particles of trehalum are coloured violet and the solution wine-red; on warming, the colour disappears, and, on again cooling, the solution assumes a deep violet colour. Trehalin is coloured reddish-violet by iodine in aqueous solution.

Trehalum is not acted on by diastase, yeast, or invertase, but always undergoes slight hydrolysis when heated even to 105°, as shown by the action of the product on Fehling's solution. It yields an acetyl derivative which melts above 240°, but shows no characteristic properties. H. G. C.

Inulase, and the Indirect Alcoholic Fermentation of Inulin. By E. Bourquelot (*Compt. rend.*, **116**, 1143—1145).—*Aspergillus niger*, when grown on a nutritive fluid containing inulin, produces a ferment capable of converting dilute solutions of inulin practically completely into levulose. This ferment is distinct from invertin and amylase, because neither of the latter has any action on inulin, and it differs from trehalase because it retains its activity after being heated at 64°. It seems to be identical with the inulase obtained by Green from one of the plants that yield inulin.

If inulin solution is mixed with inulase and beer yeast, it undergoes alcoholic fermentation, the inulase converting it into levulose, which is then attacked by the yeast. C. H. B.

Tunicin. By E. Winterstein (*Zeit. physiol. Chem.*, **18**, 43—56).—Tunicin, or animal cellulose, agrees in nearly all its properties with vegetable cellulose. It does not show greater resistance to acids than vegetable cellulose, as Berthelot stated. On hydrolysis, it yielded dextrose, and a small quantity of another sugar, which was not identified. This second sugar is, however, not galactose, mannose, or pentose. W. D. H.

Chloramines. By A. Berg (*Compt. rend.*, **116**, 887—889).—Methylchloramine is obtained by the action of sodium hypochlorite on methylamine hydrochloride. It is practically colourless, very volatile, has an extraordinarily piquant and irritating odour, and dissolves in water to the extent of about 10 per cent. by volume. Dimethylchloramine is obtained in a similar manner; it is almost colourless, has a very piquant odour, dissolves in about 8 parts of water by volume, and boils at 46° under a pressure of 765 mm.; sp. gr. at 0° = 0·986. When treated with potassium cyanide, energetic reaction takes place, and dimethylcyanamide and tetramethylcarbamide are obtained. The former boils at 163·5° under a pressure of 760 mm. The latter is formed by the hydration of a tetramethylguanidine produced by the action of the dimethylcyanamide on regenerated dimethylamine hydrochloride.

The ethylamines, when treated in a similar manner, yield analogous products.

When an aqueous solution of methylchloramine is mixed with a

solution of potassium iodide, a maroon-red, unstable precipitate is formed, which seems to be methyliodamine. Dimethylchloramine and propylchloramine behave in the same way. With the dichloramines and the monochloramines, which are less soluble in water, the reaction is less distinct.

Amyldichloramine and diamylchloramine, when distilled with water and acetic or sulphuric acid, yield only the merest traces of hypochlorous acid (compare Selivanoff, this vol., i, 305). C. H. B.

Action of Alkalis on Betaïne. By C. Scheibler (*Ber.*, **26**, 1330—1331).—Many years ago the author showed that when betaïne was treated with a large excess of potash and a little water, it gave off trimethylamine, whilst the residue yielded a base which appeared not to be identical with betaïne. Further experiments with larger quantities of betaïne, in which soda was substituted for potash, have shown, however, that, with the exception of trimethylamine, no new base is formed, the substance obtained with potash being probably impure betaïne. H. G. C.

Condensation Products of Acetone with Concentrated Sulphuric acid. By W. R. Orndorff and S. W. Young (*Amer. Chem. J.*, **15**, 249—276).—The materials employed in this investigation consisted of 6·84 kilos. of acetone and 12·6 kilos. of sulphuric acid, which were very cautiously heated together in small quantities to a temperature of 140°. The chief product was mesitylene, of which over 11·5 per cent. of the theoretical yield was obtained, and this was accompanied by a not inconsiderable quantity of isodurene. A compound boiling at 183—185°, and having the formula $C_{14}H_{22}O$, was a constant product of the reaction. It is a light, colourless, mobile liquid, with quite a marked aromatic odour; its specific gravity at 0°, compared with water at 4°, is 0·8865. From the tarry products, a hydrocarbon, boiling at 280—282°, and having the formula $C_{15}H_{20}$, was obtained. It is a viscous liquid, with a yellow colour and very little odour, and, in all probability, is a polymeride of allylene. In addition to the substances above named, propane, sulphurous anhydride, acetic acid, mesityl oxide, phorone, and sulphur compounds were produced.

Regarding the method by which mesitylene is formed from acetone, the authors are of the opinion that the acetone first unites with the sulphuric acid, forming an additive product, exactly as it does with hydrocyanic acid; the additive product loses water, yielding the acid sulphate of isopropenyl alcohol, $CH_2{:}CMe{\cdot}OH$, which, on hydrolysis, gives rise to sulphuric acid and isopropenyl alcohol, an unstable substance which rapidly changes into acetone by molecular rearrangement. When heated with concentrated sulphuric acid, however, the acid sulphate of isopropenyl alcohol would yield sulphuric acid and allylene, and 3 mols. of the latter condense to form mesitylene. The formation of mesitylene from acetone must, therefore, very closely resemble the formation of ethylene from alcohol, and, in support of this view, it may be noted that when acetone and sulphuric acid are mixed, so much heat is evolved that it is necessary to cool with ice-water the flask in which the two liquids are mixed. The mixture is

thick and oily, and has entirely lost the odour of acetone. When distilled with a large excess of water, almost all the acetone used may be recovered. G. T. M.

Ketoximes. By C. Trapesonzjanz (*Ber.*, **26**, 1426—1428).—The following ketoximes were obtained by boiling the corresponding ketones with hydroxylamine hydrochloride (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) in dilute alcoholic solution. The specific gravities given were determined at 20°, and are referred to water at 4°, being also corrected for a vacuum.

Methylbutylketoxime, NOH:CMe·CH_2Pr^{α}, is a colourless liquid, boiling at 185° under 757 mm., and at 138° under 112 mm. pressure; sp. gr. = 0·8971.

Methylisoamylketoxime, NOH:CMe·CH_2·CH_2Pr^{β}, is a colourless liquid of agreeable odour, boiling with partial decomposition at 195—196° under 761 mm. pressure; sp. gr. = 0·8881.

Ethylphenylketoxime, NOH:CEtPh, forms mono- or tri-clinic crystals, melting at 52—53°, and boils at 165° under 35 mm. pressure, at 245—246° with partial decomposition at the ordinary pressure. Pampel and Schmidt (Abstr., 1887, 252) have already obtained it, but only as an oil.

The *ethyl derivative* of *methylphenylketoxime*, NOEt:CMePh, was obtained by treating a solution of sodium in absolute alcohol successively with acetophenonoxime and ethylic iodide; it is a colourless oil, boiling at 200—202° under 43 mm. pressure; sp. gr. = 0·9997. C. F. B.

Behaviour of Trichloracetic acid at a High Temperature. By C. Engler and M. Steude (*Ber.*, **26**, 1443—1444).—When trichloracetic acid is heated at 300°, it decomposes into trichloracetic chloride, carbonic anhydride, carbonic oxide, and hydrogen chloride. This decomposition cannot be used as an argument against the rule previously given (this vol., i, 512), as, in this case, the tendency to form hydrogen chloride brings about a decomposition in another direction. A. R. L.

Application of the Dynamical Hypothesis to Keto-acid Derivatives. By C. A. Bischoff and P. Walden (*Ber.*, **26**, 1452—1460).—According to Bischoff's "dynamical hypothesis," the formation of lactones from γ-keto-acids should be influenced by the presence of alkyl radicles in the α-position. In order to test this conclusion, weighed quantities of levulinic acid and some of its alkyl derivatives were heated at 275° for different lengths of time, cooled, and titrated with sodium carbonate solution. The following results give the amounts of lactones obtained:—

Acid.	15 minutes.	30 minutes.	45 minutes.	60 minutes.
Levulinic	7·63 p. c.	13·09 p. c.	21·54 p. c.	26·57 p. c.
α-Methyllevulinic	20·48 „	29·85 „	33·90 „	48·88 „
α-Dimethyllevulinic	27·86 „	31·96 „	35·62 „	—
α-Ethyllevulinic	37·24 „	44·26 „	47·95 „	58·63 „

Ethylic acetosodacetate gives, with ethylic α-bromopropionate and α-bromonormalbutyrate, ethylic methylacetosuccinate and ethylacetosuccinate, in yields of 60 and 52 per cent. respectively. With ethylic α-bromisobutyrate, the yield of ethylic α-dimethylacetosuccinate was found to be only 4 per cent., in accordance with the dynamical hypothesis.

Ethylic methylacetosodacetate and ethylic α-bromisobutyrate, when heated with xylene in autoclaves to a pressure of 2·5 atmospheres, yielded an ethereal product, from which, by hydrolysis, tetramethylsuccinic acid and trimethylglutaric acid were obtained.

Paradimethylsuccinic acid is much less easily converted into the anhydride than antidimethylsuccinic acid. J. W.

Action of Alcohols on Lactones and Alkyl Salts. By J. WALKER (*Ber.*, **26**, 1492—1493).—In opposition to Brühl, the author shows that lactone rings have been split up by the action of alcohol alone, or together with a halogen acid. The products formed are either an ether acid, the ethereal salt of a hydroxy-acid (or corresponding halogen substituted acid), or, finally, the ethereal salt of an ether acid.

The replacement of one alkyl by another in an ethereal salt corresponds with the second of the above cases, and the author finds that ethylic oxalate, heated with excess of methyl alcohol at 160°, yields methylic oxalate, whilst this ethereal salt at the same temperature is converted by ethyl alcohol into ethylic oxalate. J. W.

Malic acid Derivatives. By P. A. GUYE (*Compt. rend.*, **116**, 1133—1136).—Active *acetylmalic anhydride*, obtained by the action of acetic chloride on carefully dried lævogyrate malic acid, melts at 58°, dissolves easily in benzene and especially in chloroform, from which it crystallises readily, but is only slightly soluble in dry ether. It rapidly absorbs moisture from the air, and forms acetylmalic acid. The rotatory power of the anhydride in chloroform solution is $[\alpha]_D = -26°$.

Active *acetylmalic acid*, obtained by the crystallisation of a concentrated solution of the anhydride in moist chloroform, has a specific rotatory power $[\alpha]_D$ of $-21·0$ to $-25·8$ in acetone, and $-10·4$ to $-10·7$ in water. When slowly heated, it softens between 120 and 125°, and melts at 130—131°. When rapidly heated, it melts at a somewhat higher temperature. The fused acid gives off acetic acid, and maleïc acid is left. It would seem, therefore, that in the conversion of malic acid into maleïc acid by the action of acetic chloride, an acetyl derivative is first formed, but is afterwards decomposed. An aqueous solution of acetylmalic acid gradually decomposes, yielding acetic and malic acids.

Propionylmalic anhydride, obtained in a similar manner, crystallises readily from chloroform, but is almost insoluble in ether. It melts at 88—89°, and its rotatory power in chloroform solution is $[\alpha]_D = -22·1°$ to $-20·4°$.

Propionylmalic acid, obtained in the same way as the acetyl derivative, is lævogyrate in chloroform solution. It crystallises from

chloroform, and at about 130° splits up into propionic and maleïc acids.

Butyrylmalic anhydride and *butyrylmalic acid* are much more difficult to isolate. The former is lævogyrate in chloroform solution, and the latter is likewise lævogyrate when dissolved in aqueous acetone.

C. H. B.

Constitution of Leucine. By B. Gmelin (*Zeit. physiol. Chem.*, 18, 21—42).—Leucine prepared from different sources is not always the same as Schulze and Likiernik (this vol., i, 309) consider. Three preparations were made (1) from yeast, (2) from caseïn, (3) from hæmoglobin. Elementary analysis gave results in each case closely corresponding to the formula $C_6H_{13}NO_2$. Their solubilities in water are however different.

	Solubility in water	
	At 19°.	At about 100°.
Preparation 1.....	1 in 28·8	1 in 15·9
„ 2.....	1 in 29·0	1 in 14·3
„ 3.....	1 in 45·8	1 in 18·7

Their action on polarised light is different. Dissolved in hydrochloric acid, $[\alpha]_D$ for preparations 1 and 2 = +17·2°, for preparation 3 = +14·3°. The melting point of leucic acid obtained from preparations 1 and 2 is 72·5°; from preparation 3, 67°. These acids also differ in rotatory power, and in the solubilities of their zinc salts.

The three fatty acids obtained correspond with isobutylacetic acid. The cause of the differences cannot be looked for in the position of the amido-group, and reasons are given for considering that one has to deal with a case of "physical isomerism."

The molecular weights of leucine, glycocine, and alanine estimated by the cryoscopic method correspond closely with those reckoned from their simplest formulæ.

W. D. H.

Hydroxylamineacetic acid. By A. Werner (*Ber.*, **26**, 1567—1571).—The author has previously shown (Abstr., 1892, 461) that benzenylchloroximeglycollic acid exists in two isomeric forms, and has now made further experiments in order to ascertain if possible the stereometric formulæ of the two isomerides. These have been unsuccessful owing to the fact that the products obtained are oils which can scarcely be distinguished from one another. They yield as a product of decomposition hydroxylamineacetic acid,

$$NH_2{\cdot}O{\cdot}CH_2{\cdot}COOH.$$

In place of the name benzenylchloroximeglycollic acid, the author prefers to employ the term benzenylchloroximeacetic acid. This acid is obtained in the manner already described from benzenylamidoximeacetic acid, the latter being preferably prepared by treating ethylic chloracetate and benzenylamidoxime with alcohol and potash, instead of soda, as the potassium salt is much less soluble. Both modifications of benzenylchloroximeacetic acid yield, on treatment with sodium ethoxide, an *ethylbenzhydroximeacetic acid*,

$$EtO{\cdot}CPh{:}N{\cdot}O{\cdot}CH_2{\cdot}COOH,$$

both products being syrupy oils which cannot be distinguished one from the other. When treated with hydrochloric acid, they are rapidly decomposed, the products being ethylic benzoate and the *hydrochloride* of *hydroxylamineacetic acid*, $NH_2{\cdot}O{\cdot}CH_2{\cdot}COOH,HCl$; the latter crystallises from alcohol in compact, white needles, and melts at 147—148°. The free acid appears to be a liquid, and is at present being further investigated.

Besides the chloro-derivative the author has converted benzenylamidoximeacetic acid into *benzenylbromoximeacetic acid*,

$$CPhBr{\cdot}N{:}O{\cdot}CH_2{\cdot}COOH,$$

benzenylfluoroximeacetic acid, $CPhF{\cdot}N{:}O{\cdot}CH_2{\cdot}COOH$, and *benzenylnitritoximeacetic acid*, $NO{\cdot}O{\cdot}CPh{\cdot}N{:}O{\cdot}CH_2{\cdot}COOH$; the first may be crystallised from hot water, and melts at 135—136°, the second forms nacreous plates, and melts at 135°, and the third crystallises in white, lustrous plates, and melts at 95—96°. In none of these cases was the formation of stereoisomerides observed. When benzenylnitritoximeacetic acid is warmed for a short time with potash, it is converted into *benzoylhydroxylamineacetic acid* (*benzhydroxamacetic acid*), $NHBz{\cdot}O{\cdot}CH_2{\cdot}COOH$ or $OH{\cdot}CPh{:}N{\cdot}O{\cdot}CH_2{\cdot}COOH$, which after crystallisation from ether melts at 135—138°. H. G. C.

Amidoxylic acids. By W. v. Miller and J. Plöchl (*Ber.*, **26**, 1545—1558).—Several methods are known by which α-amido-acids and the corresponding α-isonitroso-acids can be obtained, but hitherto none of the intermediate α-amidoxylic acids having the general formula $OH{\cdot}NH{\cdot}CHX{\cdot}COOH$ have been prepared. The authors find that the nitriles of these acids may be readily obtained by the addition of hydrogen cyanide to the oximes, and that the nitriles on treatment with hydrochloric acid yield the acids themselves. The latter contain the hydroxylamine residue $NH{\cdot}OH$, and are therefore strong reducing agents, and although they are stronger acids than the amido-acids, no salts can be obtained, for with dilute alkalis ammonia is evolved, and on addition of salts of the heavy metals reduction immediately takes place. On dry distillation, they all decompose with violent evolution of gas, forming carbonic anhydride, ammonia, pyridine bases, and often small quantities of aldehydes. Sulphuric acid cannot be employed in place of hydrochloric acid for the hydrolysis of the nitriles, as oxidation takes place simultaneously under these conditions, the corresponding α-isonitroso-acid being formed.

Propaldoxime and hydrogen cyanide combine together in the cold on remaining for two days, with formation of *α-amidoxylbutyronitrile*, $CH_2Me{\cdot}CH(NH{\cdot}OH){\cdot}CN$, which is a crystalline compound, and melts at 86—87°; when treated with cold fuming hydrochloric acid, it is converted into *α-amidoxylbutyric acid*,

$$CH_2Me{\cdot}CH(NH{\cdot}OH){\cdot}COOH,$$

which forms rhombohedral crystals, and melts at 166—167° with violent evolution of gas; the distillate contains, in addition to ammonium carbonate, a small quantity of a pyridine base, apparently

identical with parvoline, which may also be obtained by heating propaldehyde and hydroxylamine hydrochloride at 120°. The acid reduces the salts of the heavy metals quickly in the cold; it also combines directly with aldehydes forming unstable compounds which will be investigated later.

When the nitrile is treated with sulphuric acid, sulphurous anhydride is evolved, and on pouring the product into water *α-isonitrosobutyramide*, $CH_2Me{\cdot}C(NOH){\cdot}CONH_2$, separates out, and is purified by dissolving in ether and adding light petroleum. It melts at 133—135°, and on hydrolysis yields the α-isonitrosobutyric acid described by Wleügel.

Attempts to prepare the corresponding amidoxylpropionic acid from the nitrile of acetaldoxime were without success, probably owing to the fact that the acid is extremely soluble in water, and could not be isolated. If the nitrile be treated with sulphuric acid, it yields *α-isonitrosopropionamide*, $CH_2Me{\cdot}C(NOH){\cdot}CONH_2$, which crystallises in large, apparently monosymmetric tables, melts with decomposition at 178·5°, and is converted by alkalis into the known isonitrosopropionic acid.

Acetoxime readily combines with hydrogen cyanide, forming *amidoxylisobutyronitrile*, $CMe_2{\cdot}C(NOH){\cdot}CN$, which crystallises in well-developed, monosymmetric tablets, melts at 98·5°, and yields with hydrochloric acid the *hydrochloride* of *amidoxylisobutyramide*, $CMe_2(NH{\cdot}OH){\cdot}CO{\cdot}NH_2,HCl$, which separates in large crystals, and melts at 210°. Attempts to prepare the free amide and the corresponding acid were unsuccessful.

Normal butyraldoxime, which is an oil boiling at 152° under 715 mm. pressure, combines with hydrogen cyanide, forming *amidoxylvaleronitrile*, $C_5H_{10}N_2O$, which forms a spongy mass of silky crystals, melts at 102°, and has extremely active reducing properties. With hydrochloric acid, it yields *α-amidoxylvaleric acid*,

$$CH_2Me{\cdot}CH_2{\cdot}CH(NOH){\cdot}COOH,$$

which crystallises in rhombic plates, sinters at 150°, melts at 156°, and is also a very strong reducing agent. With sulphuric acid, the nitrile is converted into *isonitrosovaleramide*, $C_5H_{10}N_2O_2$; the latter crystallises in slender needles, melts at 131°, and may be converted in the usual manner into α-isonitrosovaleric acid.

Isovaleraldoxime yields with hydrogen cyanide *amidoxylisocapronitrile*, $C_6H_{12}N_2O$, crystallising in delicate, white threads, and melting at 103—104°. The corresponding *α-amidoxylcaproic acid*,

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH{\cdot}OH){\cdot}COOH,$$

forms vitreous prisms, and melts with decomposition at 151°. The *α-isonitrosoisobutylacetamide*, $C_6H_{12}N_2O_2$, obtained by the action of sulphuric acid on the nitrile, separates in well developed tablets, and melts at 146—147°, the corresponding acid melting at 159—160°. Œnanthaldoxime forms *α-amidoxylcaprylonitrile*, $C_8H_{16}N_2O$, which is a white, paper-like mass, and melts at 92—93°. *α-Amidoxylcaprylic acid* itself crystallises in colourless rhombohedra, melts at 168°, and has strong reducing properties. *α-Isonitrosocaprylamide*, prepared

from sulphuric acid and the nitrile, separates from water in vitreous needles, and melts at 138—139°. H. G. C.

Thionylamines. By A. MICHAELIS (*Annalen*, **274**, 173—186; compare Abstr., 1891, 310 and 715).—Introductory and general remarks (see next abstract and this vol., i, 515). Primary aliphatic amines are converted into thionylamines on treatment in ethereal solution with thionyl chloride. The thionylamines are also formed by the interaction of the aliphatic amines and thionylaniline.

Aromatic amines containing the substituents Cl, Br, I, Fl, NO_2, OR, and COOR (R being an alkyl) yield thionylamines when dissolved in benzene and treated with thionyl chloride; those containing the substituents OH and COOH do not yield thionylamines.

The compounds obtained by the interaction of water and the thionylamines are thus represented by the author:—

$R{\cdot}NH{\cdot}SO_2H$, Alkylthionamic acid. $R{\cdot}NH{\cdot}SO_2{\cdot}NH_3R'$; Alkylamine salt of last acid.

whilst those obtained by the interaction of aldehydes and thionylamines are represented thus:—

$SO_2H{\cdot}NR{\cdot}CHX{\cdot}OH$, Aldehydealkylthionamic acid. $NH_3R'{\cdot}SO_2{\cdot}NR{\cdot}CHX{\cdot}OH$. Alkylamine salt of last acid.

Thionyl chloride is prepared either by the action of sulphurous anhydride on phosphoric chloride (Schiff) or by that of sulphuric anhydride on sulphur dichloride. The last method, when carefully carried out, yields 80 per cent. of the theoretical quantity of thionyl chloride, and the materials are much cheaper than those employed in the first-mentioned method; it, however, necessitates greater attention. A. R. L.

Thionylamines of the Aliphatic Series. By A. MICHAELIS and O. STORBECK (*Annalen*, **274**, 187—196).—*Thionylmethylamine*, SO:NMe, is prepared by adding methylamine to a cooled solution of thionylaniline in dry toluene, and allowing the mixture to remain some time at the ordinary temperature. It is a colourless or faintly yellow fuming liquid having an odour recalling that of bleaching powder, boils at 58—59°, and decomposes into methylamine and sulphurous anhydride when shaken with water. The yield is small, and besides aniline, a solid amorphous bye-product is also formed. Thionylethylamine (Abstr., 1891, 718) may be prepared in a similar manner.

Thionylpropylamine, SO:NPr, is obtained by the action of thionyl chloride on an ethereal solution of propylamine. It boils at 104°, and resembles its lower homologue, but is more stable towards water.

Thionylisobutylamine, $SO{:}N{\cdot}CH_2{\cdot}CHMe_2$, prepared in a similar manner to the last-named compound, is a colourless liquid having a penetrating, sweetish odour; it exerts a corrosive action on the skin, boils at 116°, and is decomposed by water.

Thionylamylamine, $SO{:}N{\cdot}C_5H_{11}$, is a liquid having a less penetrating

odour than the analogues already described; it decomposes when distilled at the ordinary pressure, and, when shaken with water, boils at 90° under a pressure of 65 mm., and at 80° under a pressure of 45 mm.

Ethylthionamic acid ("*ethylamine sulphite*"), NH_2Et,SO_2 ($NHEt{\cdot}SO_2H$?), separates as a white, hygroscopic powder when dry sulphurous anhydride is led into an ethereal solution of ethylamine. The corresponding propylamine and isobutylamine derivatives were also prepared. The isobutylamine compound loses sulphurous anhydride on remaining in the desiccator and furnishes *isobutylamine isobutylthionamate*, $2NH_2{\cdot}C_4H_9,SO_2$, probably $C_4H_9{\cdot}NH{\cdot}SO_2{\cdot}NH_2{\cdot}C_4H_9$. *Amylthionamic acid* behaves in an analogous manner.

Benzaldehydepropylthionamic acid, $NH_2Pr^{\alpha},SO_2,PhCHO$, probably $= SO_2H{\cdot}NPr^{\alpha}{\cdot}CHPh{\cdot}OH$, separates in white crystals on addition of benzaldehyde to an alcoholic solution of thionylpropylamine or of propylthionamic acid. It melts at 96°, its aqueous solution has an acid reaction, and on boiling it the compound is decomposed. When aniline is added to its aqueous solution, a *compound* having probably the constitution $NH_2Ph{\cdot}SO_2{\cdot}NPr^{\alpha}{\cdot}CHPh{\cdot}OH$, is precipitated in crystals; it melts at 145°, and is decomposed by mineral acids with the evolution of sulphurous anhydride.

Benzaldehydeisobutylthionamic acid, $NH_2{\cdot}C_4H_9,SO_2,PhCOH$, melts at 116—117°, and, when treated with aniline, yields the compound $C_{17}H_{24}N_2SO_3$, melting at 160°.

Benzaldehydeamylthionamic acid, $NH_2{\cdot}C_5H_{11},SO_2,PhCOH$, melts at 113°, and, on treatment with aniline, gives the *compound* $C_{18}H_{26}N_2SO_3$, melting at 138°. A. R. L.

Syntheses with Aluminium Chloride. By P. Genvresse (*Compt. rend.*, **116**, 1065—1067).—When 500 grams of normal propyl bromide is added gradually to a boiling mixture of 700 grams of benzene free from thiophen and 40 grams of aluminium chloride, and the product is washed with water, dried over calcium chloride, and fractionated, a mixture of normal propylbenzene and isopropylbenzene is obtained. It would seem that the proportion of the latter would be reduced by the use of as small a proportion of aluminium chloride as possible. C. H. B.

Iodoso- and Iodoxy-compounds. By C. Willgerodt (*Ber.*, **26**, 1307—1313; see also this vol., i, 149).—Iodosobenzene, when boiled with water, either in the presence or absence of air, is converted into iodoxybenzene and iodobenzene. When iodosobenzene is treated with an aqueous solution of potassium iodide, only a partial decomposition takes place. In the presence of acetic or hydrochloric acid, however, the reaction is quantitative and iodine is liberated. The titration of this solution with sodium thiosulphate gives a greater quantity of oxygen than that required by theory, indicating the presence of iodoxybenzene in the iodosobenzene.

Phenyl iodochromate, $C_6H_5{\cdot}I{:}CrO_4$, is obtained by adding chromic acid to an acetic acid solution of iodosobenzene. It is a yellow compound which reddens on drying, explodes at 66—67°, and liberates

the theoretical quantity of iodine from a solution of potassium iodide containing sulphuric acid.

The nitrate, $IPh(NO_3)_2$, has been obtained in thick, yellow tablets belonging to the monoclinic system; $a : b : c = 2{\cdot}3124 : 1 : 1{\cdot}2784$, $\beta = 51° 45'$.

Iodoxybenzene, $C_6H_5{\cdot}IO_2$, when treated with hydrochloric acid in aqueous solution, is converted into iodosobenzene hydrochloride, and chlorine is evolved. When treated with hydrogen peroxide, it is converted into iodobenzene, and oxygen is liberated. With chromic acid in aqueous solution, it yields iodobenzene; in acetic acid solution, however, it yields a yellow compound which explodes at 73°.

Metanitriodobenzene dichloride, $NO_2{\cdot}C_6H_4{\cdot}ICl_2$, is obtained by treating a cold chloroform solution of metanitriodobenzene with chlorine. It crystallises in large, yellow plates or prisms, decomposes at 100—102°, and decomposes when dissolved in acetic acid or alcohol, whereby the alcohol is converted into aldehyde.

Metanitriodosobenzene, $NO_2{\cdot}C_6H_4{\cdot}IO$, is obtained by the action of dilute sodium hydroxide on the preceding compound. It sinters at 180° and decomposes at 190—195°. The *acetate*, $NO_2{\cdot}C_6H_4{\cdot}I(OAc)_2$, crystallises in almost colourless prisms, and melts without decomposition at 150—155°. The *chromate* is a red, microcrystalline powder, and explodes at 95°.

Metanitriodoxybenzene, $NO_2{\cdot}C_6H_4{\cdot}IO_2$, is obtained together with nitriodobenzene by boiling the iodoso-compound with water. It crystallises in colourless lamellæ, and explodes at 215°.

E. C. R.

Orthiodosobenzene and Orthochloriodoxybenzene. By C. Willgerodt (*Ber.*, **26**, 1532—1534).—When a well-cooled solution of orthiodobenzene is treated with chlorine, *orthochlorophenyl iodochloride*, $C_6H_4Cl{\cdot}ICl_2$, separates as a pale yellow, crystalline powder, which decomposes with violent evolution of gas at 95—98°, and quickly darkens on exposure to air and light. On treatment with dilute soda, it is converted into *orthochloriodosobenzene*, $C_6H_4Cl{\cdot}IO$, which separates out as a very pale yellow powder, and cannot be recrystallised from any solvent. It explodes without any report at 83—85°, and on treatment with acetic acid yields the *diacetate*, $C_6H_4Cl{\cdot}I(OAc)_2$, which crystallises in colourless, transparent prisms, becomes plastic at 125°, and melts at 140°. The *chromate*,

$$C_6H_4Cl{\cdot}I{:}CrO_4,$$

is a brownish-red powder which decomposes at 56—57° with a slight report.

When orthochloriodosobenzene is boiled with water, orthochloriodobenzene distils over, and the hot solution on cooling deposits *orthochloriodoxybenzene*, $C_6H_4Cl{\cdot}IO_2$, in small, white needles, which decompose with a sharp report at 203°. It also yields a *chromate* on treatment with acetic acid and chromic acid solutions.

H. G. C.

Iodoso-compounds. By P. Askenasy and V. Meyer (*Ber.*, **26**, 1354—1370; compare Abstr., 1892, 1460).—Some of the properties

assigned by Willgerodt (this vol., i, 149) to iodosobenzene differ so much from those observed by Meyer and Wachter for iodosobenzoic acid that the authors have repeated Willgerodt's experiments, and have obtained different results. Thus they find that iodosobenzene liberates quantitatively 2 atoms, and iodoxybenzene 4 atoms, of iodine from potassium iodide, whereas Willgerodt found that the former set free approximately 1 atom of iodine, and the latter had no action on the iodide. This difference is probably partly due to the fact that Willgerodt did not acidify the potassium iodide solution with acetic acid. They are also unable to confirm Willgerodt's statement that iodosobenzene is converted into iodoxybenzene by the action of the oxygen of the air; the latter, in reality, takes no part in the reaction, but the iodobenzene on heating is converted into iodobenzene and iodoxybenzene:

$$2C_6H_5IO = C_6H_5I + C_6H_5{\cdot}IO_2.$$

The explosion of iodosobenzene observed by Willgerodt is in reality due to the iodoxybenzene which is formed when it is heated.

Owing to the different melting points of the various specimens of iodosobenzoic acid, the authors thought it possible that a mixture of two isomeric acids might be present, but all yield the same crystalline acetyl derivative, and must therefore be identical.

Iodosobenzoic acid may be prepared from pure orthiodobenzoic acid either by the action of fuming nitric acid or of acid potassium permanganate, and also by acting on it with chlorine in chloroform solution and treating the dichloride with alkalis. The colourless acid dissolves in alkalis and sodium carbonate solution, forming deep yellow solutions which are reprecipitated by mineral acids. Its conductivity has been found by Ostwald to be $k = 0{\cdot}00006$, and it is, therefore, one of the feeblest known acids. The *sodium* and *calcium* salts are amorphous, and the *silver* salt forms a yellow precipitate which is very explosive when dry; no ethereal salts could be prepared.

On aromatic amido-compounds, iodosobenzoic acid acts as an oxidising agent yielding amorphous colouring matters, and with ethylamine, it forms salicylic acid. When treated with potassium permanganate in alkaline solution, it is partially reduced to form iodobenzoic acid, and partially oxidised to iodic acid and iodoxybenzoic acid; the latter compound will be described later. Boiling aqueous alkalis attack the acid very slightly with formation of a small quantity of iodate, but with alcoholic soda, it yields salicylic acid, the oxygen simultaneously evolved acting on the alcohol with formation of aldehyde.

In order to decide if possible between the two possible formulæ, $IO{\cdot}C_6H_4{\cdot}COOH$ and $C_6H_4<^{I(OH)}_{CO}>O$, the authors treated iodosobenzoic acid with acetic anhydride, and obtained an *acetyl* derivative, $C_7H_4O_3IAc$, crystallising in apparently monosymmetric prisms, and melting at 166—167°. The formation of an acetyl compound appeared to support the second of the above formulæ, as no case has been hitherto observed in which, by the direct action of acetic an-

hydride, the hydrogen of the carboxyl group is displaced by the acetyl group. It was found, however, on further investigation that paradimethylamidobenzoic acid also yields an acetyl derivative under similar conditions, and therefore no conclusions as to the constitution of iodosobenzoic acid can be drawn from this reaction. The acetyl compound of the dimethamidobenzoic acid, $NMe_2 \cdot C_6H_4 \cdot COOAc$, crystallises in needles, and melts at 109°.

All attempts to obtain iodoso-derivatives from meta- and para-iodobenzoic acid have been without success. Of the two iodoparatoluic acids, the one in which the iodine atom occupies the ortho-position to the carboxyl group yields an iodoso-derivative similar to iodosobenzoic acid, but the isomeric acid does not yield a corresponding compound. If, however, pariodobenzoic acid be previously nitrated, it may be converted by the further action of fuming nitric acid into an iodoso-derivative, $IO \cdot C_6H_3(NO_2) \cdot COOH$, which is an intensely yellow substance, insoluble in the usual solvents. When treated with alcoholic soda, it is converted into sodium iodate, sodium nitrobenzoate, and sodium nitriodobenzoate. In a similar manner the iodoparatoluic acid, which does not yield an iodoso-compound directly, may be made to do so by previous nitration. H. G. C.

Metallic Compounds of the Benzene Series. By G. Perrier (*Compt. rend.*, **116**, 1140—1143).—When phenylic benzoate, resorcinol or quinol dibenzoate, or phenylic phthalate is boiled with aluminium chloride and carbon bisulphide, a crystalline compound, almost insoluble in carbon bisulphide, separates on cooling. Phenylic benzoate yields colourless crystals of the compound $(C_6H_5 \cdot COOPh)_2,Al_2Cl_6$, which dissociates somewhat rapidly when exposed to air, and is at once split up into its constituents by water. Resorcinol and quinol dibenzoates yield compounds of the formula $2C_6H_4(OBz)_2,Al_2Cl_6$. The same compounds are formed when the chlorides of the acids of the benzene series are heated with the phenols in presence of carbon bisulphide and aluminium chloride.

Under the latter conditions, β-naphthol yields golden-yellow crystals of the composition $2OBz \cdot C_{10}H_6 \cdot OH,Al_2Cl_6$. It dissociates slightly when exposed to air, and, when treated with water, it yields aluminium chloride and a benzoylnaphthol. The latter crystallises from ether-alcohol in pale yellow, silky needles which melt at 141°, and sublime easily. It dissolves in alkalis, and is reprecipitated by acids. Its sodium salt crystallises in orange plates, and the ammonium salt in yellow needles. Benzoylnaphthol combines with phenylhydrazine.

Other naphthols behave in the same way. Chlorides of the acids of the acetic series likewise yield ketonic phenols when boiled with naphthols in presence of aluminium chloride, and the same reaction takes place even when the phenol has only one nucleus; whereas, under the same circumstances, chlorides of the acids of the benzene series yield only ethereal salts.

Phenol combines with aluminium chloride to form large, colourless lamellæ; thymol yields rose-white crystals, very unstable when exposed to air; and β-naphthol yields a greenish-yellow, crystalline

powder. All these products, when treated with water, split up into aluminium chloride and the original phenol.

Ferric chloride behaves in the same way, but the results are less distinct. C. H. B.

Action of Formaldehyde on Nitrosodimethylaniline. By J. Pinnow and G. Pistor (*Ber.*, **26**, 1313—1315).—When finely-powdered nitrosodimethylaniline is heated with formaldehyde on the water-bath, a violent reaction takes place, and the product, when precipitated with water, yields tetramethyldiamidoazoxybenzene, $ON_2(C_6H_4{\cdot}NMe_2)_2$, which melts at 243° (uncorr.), and yields paramidodimethylaniline when boiled with tin and hydrochloric acid, and tetramethyldiamidoazobenzene when boiled with alcoholic potash and zinc dust.

The mother liquors of the preceding compound contain the *formyl* derivative of *paramidodimethylaniline*, $HCO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, which is separated by fractional precipitation with salt. It crystallises in silvery leaflets, melts at 108°, and, when boiled with hydrochloric acid or alkalis, yields formic acid and paramidodimethylaniline. The *picrate* melts at 188°. The *mercurochloride* melts at 171°.

E. C. R.

Action of Phenylhydrazine on Diazobenzene. By A. Wohl (*Ber.*, **26**, 1587—1589).—In view of the recent paper of Curtius (this vol., i, 463), the author gives an account of the investigation he has made on the action of phenylhydrazine on diazobenzene, although this is at present incomplete.

If phenylhydrazine acetate and diazobenzene acetate are allowed to interact in dilute acetic acid solution, a precipitate is formed, which may be purified by crystallising from ether and washing with alcohol, and then forms pale yellow crystals melting at 71° with decomposition. It explodes when touched with a warm glass rod, and, on warming in alcoholic solution, gives off nitrogen, the odour of phenylhydrazine being also perceptible. It appears to have the formula $C_{12}H_{12}N_4$, and is probably formed directly from phenylhydrazine and diazobenzene with elimination of water. H. G. C.

Ethylic Azobenzenecyanacetate. By F. Krückeberg (*J. pr. Chem.* [2], **47**, 591—592).—The two modifications of this compound melt at 125° (α-) and at 82° (β-) respectively; the substance which melts at 106—108° (this vol., i, 210) is probably a molecular mixture of the two. Both modifications are optically inactive. The benzoyl derivative (*loc. cit.*) is hydrolysed by potash to potassium ethylic azobenzeneacetate; the ethyl derivative (*loc. cit.*) under the same treatment yields a salt of ethylazobenzenecyanacetic acid,

$$N_2EtPh{:}C(CN){\cdot}COOH$$

(m. p. 147°). The reaction between ethylic chlorocarbonate and potassium ethylic azobenzenecyanacetate yields the carboxethyl derivative, $COOEt{\cdot}N_2Ph{:}C(CN){\cdot}COOEt$.

The compounds obtained by the action of ortho- and of para-diazotoluene chloride, respectively, on ethylic cyanacetate also occur each in two forms: ethylic α-azorthotoluenecyanacetate melts at 85°, the

β-derivative at 133°; ethylic α-azoparatoluenecyanacetate melts at 118°, the β-derivative at 74°.

The study of the action of nitrous acid on these substances is not yet complete. A. G. B.

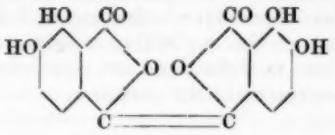
Stereoisomerism of the Benzhydroxamic acids. By A. WERNER (*Ber.*, **26**, 1561—1567; compare Abstr., 1892, 461).—This paper consists chiefly of a defence of the author's nomenclature and results against Lossen's criticisms (Abstr., 1892, 711). He has repeated the portion of his work referring to the determination of the stereometric formulæ of the two ethylbenzhydroximic acids, and has confirmed his previous results in all respects but one, namely, the formula of the phosphate of the "anti-" acid. This was first given as $PO(O{\cdot}N{:}CPh{\cdot}OEt)_3 + H_2O$, but it is now found that the substance is anhydrous.

In his first experiments, the author was unable to obtain the benzoyl derivative of ethylsynbenzhydroximic acid, as by the action of benzoic chloride and soda, the acid is converted into the "anti-" benzoyl compound. If, however, the soda be replaced by potash, the "syn-" derivative may readily be obtained, and, after crystallisation from ether, melts at 58°. H. G. C.

Constitution of Gallic Blue or Tannin-indigo. By P. CAZENEUVE (*Compt. rend.*, **116**, 884—887).—When nitrosodimethylaniline is heated with gallanilide in presence of acetic acid, alcohol, or other solvent, it yields a brilliant olive-green colouring matter, insoluble in water or in alkalis, but soluble in aniline, from which it can be crystallised. This compound dissolves in concentrated sulphuric acid, forming a blue-violet solution, and, on addition of water, a deep violet precipitate is obtained. When 5 parts of this olive-green product is heated with 20 parts of alcohol and 20 parts of a 40 per cent. solution of sodium hydrogen sulphite, a soluble sodium salt of a sulphonic derivative is obtained. The sulphonic acid can also be formed by the direct action of sulphuric acid. The sodium salt has the composition $NaSO_3{\cdot}C_{20}H_{17}N_2O_4Cl$. The relation of the sulphonic derivative and the insoluble green compound to gallocyanine is shown by graphic formulæ. Gallocyanine is an oxindophenol, and gallic blue is derived from it by the substitution of $NH{\cdot}C_6H_5$ for an oxygen atom in the carboxyl group. C. H. B.

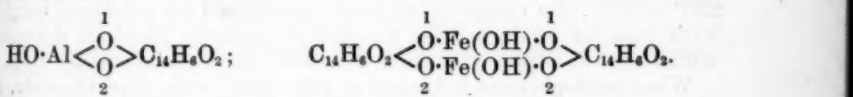
The Theory of the Formation of Coloured Compounds with Mordants. By C. LIEBERMANN (*Ber.*, **26**, 1574—1578).—The author has shown, in conjunction with Bistrzycki (this vol., i, 371), that numerous derivatives of opianic acid are coloured, and also that certain of them, such as tetramethoxydiphthalyl and bisdimethoxymetaindolone, on treatment with concentrated sulphuric acid, yield colouring matters which unite with mordants, forming coloured lakes. The action of sulphuric acid consists in the elimination of the methyl groups, and the same reaction may be brought about by heating with concentrated hydriodic acid. Tetramethoxydiphthalyl is thus converted into the corresponding tetrahydroxydiphthalyl, which has been

previously investigated by Goldschmiedt and Egger (Abstr., 1891, 1371), who have conclusively shown that its constitution is represented by the formula



Each pair of hydroxyl groups occupies the ortho-position, thus again confirming the supposition of the author and Kostanecki (Abstr., 1888, 274; 1889, 868) that, with the phenol and acid colouring matters, only those compounds containing at least two hydroxyl groups in the ortho-position yield coloured derivatives with mordants.

Hitherto no explanation has been given of this property, and the author suggests that the reason is to be found in the fact that only in this case is the hydrogen of both hydroxyl groups capable of combining with the hydroxyl groups attached to one and the same metallic atom (such as Al) or with hydroxyl groups attached to a double atom (such as Fe·Fe). Alizarin red and violet would then have the following formulæ:—



This property of the orthohydroxy-compounds would be in strict accordance with their general behaviour, inasmuch as they so frequently undergo condensation with formation of ring derivatives. The fact that the properties of the metal are often masked in the coloured derivatives would be also then explained, as this frequently occurs when the metal is present in the molecule in a closed chain of atoms. H. G. C.

Some Anilides and Toluidides which exist in two Modifications. By C. A. Bischoff and P. Walden (*Ber.*, **26**, 1461—1462).—By the action of phosphoric chloride on compounds of the type OH·CHX·CO·NHY [X = an aliphatic alkyl; Y = an aromatic alkyl], chloro-derivatives are obtained which, when treated with water, lose chlorine, and pass into substances XCO·CO·NHY or, as they are soluble in alkali, XCO·C(OH):NY (compare Nef, Abstr., 1892, 1440). When the alkaline solutions of these compounds are acidified, polymeric substances of higher melting point and twice as great molecular weight are precipitated. The following compounds have been obtained up to the present, X = CH_3:—*Pyruvic anilide* melts at 104°, and yields a *polymeride* melting at 196°; *pyruvic orthotoluidide* melts at 71°, and yields a *polymeride* melting at 174°; *pyruvic paratoluidide* melts at 109°, and yields a *polymeride* melting at 201°. X = C_2H_5:—The *paratoluidide* melts at 131°, and yields a *polymeride* melting at 192°. Two new hydrated *pyruvic orthotoluidides*,

$$CMe(OH)_2CO\cdot NH\cdot C_6H_4Me,$$

insoluble in aqueous alkali, exhibit the same relation. A modification melting at 111° is formed when the chlorinated intermediate product is distilled under diminished pressure and decomposed with water; whilst, when the chloro-derivative is decomposed directly with water, a compound having twice the molecular weight and melting at 177° is obtained; these two modifications are not interconvertible. Nef promises to further investigate the matter. A. R. L.

Condensation of Acetophenone on heating alone or with Zinc Chloride. By C. ENGLER and L. DENGLER (*Ber.*, **26**, 1444—1449; compare Delacre, Abstr., 1892, 993).—When acetophenone is boiled in a reflux apparatus for 16 days, 20 per cent. of unaltered substance passes over on distillation, and the residue consists of 20 per cent. of dypnone, 45 per cent. of triphenylbenzene, and a small quantity of a compound melting at 109°. The latter proves to be *αβ'-diphenylfurfuran*, $\begin{matrix}\text{CPh:CH}\\ |\\ \text{CH:CPh}\end{matrix}\!>\!\text{O}$, and may be prepared by heating dypnone with nitrobenzene at 190°. It forms white leaflets, having a bluish fluorescence; its solutions also exhibit fluorescence. By heating acetophenone in a sealed tube at temperatures varying from 290° to 370°, the compounds already mentioned are produced together with gaseous products; the amount of dypnone obtained decreases, whilst that of triphenylbenzene increases, as the temperature rises.

When acetophenone is heated at 130—170° with zinc chloride, the products are dypnone and triphenylbenzene, but no diphenylfurfuran; at higher temperatures benzoic acid is also formed, apparently through the presence of zinc oxychloride. A. R. L.

Behaviour of Organic Acids and Ethereal Salts at High Temperatures. By C. ENGLER and E. LÖW (*Ber.*, **26**, 1436—1443). —In continuation of previous work on the formation of mineral oil (Abstr., 1888, 928; 1889, 586), the authors describe experiments having for their object the explanation of the occurrence of aromatic hydrocarbons in the mineral oil. Some experiments were carried out in a sealed tube bent at an obtuse angle; one part of the tube was heated in a furnace, the other portion projecting downwards beyond the furnace, so that distillation proceeded at a high pressure from the hot to the cold portion of the tube. Other experiments were made in a sealed tube heated in the usual manner. The pressure was approximately measured by means of small capillary tubes, closed at one end, the compression of the inclosed air being measured by the movement of a globule of mercury. The gaseous products were removed from time to time when the pressure was excessive.

When phenylacetic acid is heated in an ordinary sealed tube at 355—375°, toluene, carbonic anhydride, dibenzyl ketone, and a small quantity of carbonic oxide are formed. By heating the acid at 375° in an exhausted vessel in so small a quantity that no excess of pressure is produced, the same decomposition occurs, so that pressure has no direct influence on the reaction. It is noteworthy that phenylacetic acid is a normal decomposition product of putrefactive

proteïds, and the presence of benzenoïd hydrocarbons in mineral oil may not therefore be exclusively due to a pyrogenetic process.

Benzoic and acetic acids undergo slight decomposition only when heated at 390°; cinnamic acid is partially decomposed at 320°. Ethylic acetate is unaltered at 290°; methylic phenylacetate decomposes at 360° into toluene, methyl alcohol, and gaseous products; methylic benzoate undergoes very little decomposition at 380—400°, but ethylic benzoate is decomposed at 360° into benzoic acid and ethylene, and the amylic salt at 340—350° into benzoic acid and amylene.

The authors believe that their experiments show that the acids decompose the more readily the more negative the nature of their non-carboxylic residues. The tendency of the hydrogen of the carboxyl group to combine with methyl in acetic acid is much less than it is to combine with the group CH_2Ph in phenylacetic acid.

A. R. L.

New Synthesis of Allocinnamic acid. By C. Liebermann (*Ber.*, **26**, 1571—1574).—Claisen and Crismer have shown that when benzalmalonic acid, $CHPh{:}C(COOH)_2$, is heated at about 195°, it splits up into carbonic anhydride and cinnamic acid. The author has repeated the experiment, heating the acid in quantities of 20—25 grams in an oil bath at 195° for 6—9 minutes, and finds that under these conditions about 5—6 per cent. of the benzalmalonic acid is converted into allocinnamic acid, the remainder being converted into cinnamic acid.

Benzalmalonic acid has in all probability the stereometric formula $\begin{matrix} Ph\cdot C\cdot H \\ \| \\ COOH\cdot C\cdot COOH \end{matrix}$, and the formation of allocinnamic acid in this manner is therefore an additional proof of the supposition that the two acids are stereoisomerides.

H. G. C.

Condensation of Cinnamic acid with Hydrocarbons. By W. Karsten (*Ber.*, **26**, 1579—1583).—Cinnamic acid undergoes condensation with toluene and metaxylene in presence of sulphuric acid in the same manner as with benzene (Abstr., 1891, 1484; 1892, 848, 1228), forming phenyltolylpropionic and phenylxylylpropionic acids. *Phenyltolylpropionic acid*, $C_6H_4Me\cdot CHPh\cdot CH_2\cdot COOH$, is a light, white powder insoluble in water, and melts at 145—146°; its *calcium* salt forms microscopic, white plates, and its *silver* salt a white precipitate susceptible to light, whilst the *methylic* salt is an oil. When treated with permanganate in alkaline solution, the acid is converted into phenyl paratolyl ketone, $COPh\cdot C_6H_4Me$, and parabenzoylbenzoic acid, the formation of this ketone proving that the original acid is β-phenyl-β-paratolylpropionic acid.

Phenylxylylpropionic acid, $C_6H_3Me_2\cdot CHPh\cdot CH_2\cdot COOH$, is a crystalline precipitate; it melts at 111—112°, and yields *calcium* and *silver* salts having the formulæ $(C_{17}H_{17}O_2)_2Ca$ and $C_{17}H_{17}O_2Ag$ respectively. On oxidation, it does not give a ketone, but, according to the length of time allowed for the oxidation, yields compounds in which one or both of the methyl groups are oxidised to carboxyl. The first compound, *phenylcarboxytolylpropionic acid*,

$$COOH\cdot C_6H_3Me\cdot CHPh\cdot CH_2\cdot COOH,$$

is a white, crystalline powder, and melts at 252°; the *silver* salt is a white, flocculent precipitate somewhat susceptible to light. *Phenyldicarboxyphenylpropionic acid*, $C_6H_3(COOH)_2 \cdot CHPh \cdot CH_2 \cdot COOH$, may be crystallised from hot water, and melts at 218° with decomposition; it forms *calcium* and *barium* salts having the formulæ $(C_{17}H_{11}O_6)_2Ca_3$ and $(C_{17}H_{11}O_6)_2Ba_3$. H. G. C.

Phenylic and α- and β-Naphthylic Salicylates. By H. Eckenroth and M. Wolf (*Ber.*, **26**, 1463—1470).—*Phenylic dibromosalicylate* [OH : COOPh : Br_2 = 1 : 2 : 4 : 6] is obtained, together with the *monobromo*-derivative (m. p. 98°), when bromine is added to an alcoholic solution of phenylic salicylate in the cold; at a higher temperature, in presence of excess of bromine, the dibromo-derivative alone is formed. It crystallises in white, silky needles, melts at 128° (uncorr.), and yields dibromosalicylic acid (m. p. 219°) on hydrolysis with soda. *α-Naphthylic dibromosalicylate* melts at 155°, and the *β-naphthylic* derivative melts at 191°.

α-Naphthylic nitrosalicylate [OH : COO·$C_{10}H_7$: NO_2 = 1 : 2 : 4] is obtained, together with the *dinitro*-derivative

$$[OH : COO \cdot C_{10}H_7 : (NO_2)_2 = 1 : 2 : 4 : 6],$$

by nitrating a dilute solution of α-naphthylic salicylate in glacial acetic acid at 0°. The dinitro-compound, which melts at 192°, separates in yellow leaflets, whilst the mononitro-compound remains in the mother liquor. The corresponding *β-naphthylic* derivatives are obtained in the same manner. The *mononitro*-compound melts at 201°, and the *dinitro*-compound melts at 254°.

Phenylic salicylate phenylcarbamate, $NHPh \cdot CO \cdot O \cdot C_6H_4 \cdot COOPh$, is obtained by heating phenylic salicylate with phenylic cyanate in a sealed tube at 160°, or, better, by heating carbanilide with phenylic salicylate in a reflux apparatus; it melts at 241—242°. The corresponding *α-naphthylic* compound melts at 244°, and the *β-naphthylic* derivative melts at 268°.

Phenylic acetylsalicylate, $OAc \cdot C_6H_4 \cdot COOPh$, is obtained by heating phenylic salicylate with acetic anhydride in a reflux apparatus; it melts at 98°. The *α-naphthylic* compound melts at 91°, and the *β-naphthylic* compound melts at 136°.

When phenylic or the naphthylic salicylates are heated with alcoholic ammonia in a sealed tube at 100°, salicylamide is formed.

β-Naphthylic dinitrodibromosalicylate

$$[OH : COO \cdot C_{10}H_7 : (NO_2)_2 : Br_2 = 1 : 2 : 3 : 5 : 4 : 6]$$

was prepared by adding the calculated amount of nitric acid to a boiling solution of the dibromo-compound in glacial acetic acid. The product crystallised in reddish needles, melted between 248° and 262°, and was not obtained pure. It is sparingly soluble in all solvents. *Dinitrodibromosalicylic acid* obtained on hydrolysis forms yellowish needles, and melts at 162°.

Clemm (*Ber.*, **3**, 126) has shown that a chlorine atom in a contiguous position to a nitro-group is readily replaced by other radicles. When the above-described β-naphthylic dinitrodibromo-

salicylate is heated with aniline and a little alcohol in a reflux apparatus, the *compound* $NHPh{\cdot}C_6Br(NO_2)_2(OH){\cdot}COO{\cdot}C_{10}H_7$ is obtained. It crystallises in brown, lustrous needles, and melts at 222°. Attempts to replace the second bromine atom were unsuccessful.

A. R. L.

Action of Phthalic Chloride on Trinitraniline. By H. A. Rouffaer (*Rec. Trav. Chim.*, **11**, 275—277).—By heating these two substances together at 160°, *trinitrophenylphthalimide*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N{\cdot}C_6H_2(NO_2)_3,$$

is obtained in monoclinic crystals melting at 251°. C. F. B.

Action of Thionyl Chloride on Benzylamine. By A. Michaelis and O. Storbeck (*Annalen*, **274**, 197—200; see this vol., i, 504).—Benzylamine does not yield a thionylamine when treated in ethereal solution with thionyl chloride, but the products of the reaction are benzylamine hydrochloride, benzaldehyde, and a compound containing sulphur. By the action of thionylaniline on benzylamine, there is formed benzilidenaniline, which results from the combination of the primary products benzaldehyde and aniline. A compound was also isolated giving numbers on analysis intermediate between those required for ammonium thiosulphate and ammonium trithionate.

A. R. L.

Thionylamines of the Aromatic Series. By A. Michaelis and others (*Annalen*, **274**, 200—266; see this vol., i, 504).—The sp. gr. of thionylaniline at 15° is 1·2360. The compound yields aniline and hydrogen sulphide or sulphur, on reduction with zinc-dust and acetic acid. When chlorine is passed into a solution of thionylaniline in light petroleum, trichloraniline (m. p. 78°) is formed; the action of chlorine is therefore analogous to that of bromine (Abstr., 1891, 716). A solution of *chlorothionylaniline*, $NPh{:}SCl_2$, appears to be formed when thionylaniline is dissolved in carbon tetrachloride, and the solution heated with phosphoric chloride; the compound cannot be isolated, as it decomposes in contact with moisture into thionylaniline, or in contact with hydrogen chloride into parachloraniline hydrochloride. Azobenzene is obtained by the action of thionylaniline on an ethereal solution of hydrazobenzene. When thionylaniline is heated with aniline in a sealed tube at 200°, the chief product is a dark-blue powder having a coppery shimmer; it is almost insoluble in alcohol, and may have the constitution $NH<\begin{matrix}O\text{—}\\C_6H_4\end{matrix}>S(C_6H_4{\cdot}NH_2)_2$, and is, perhaps, identical with the colouring matter obtained by Bennert (*Chem. Centr.*, 1889, 656) by the action of sulphuric anhydride on aniline. Similar substances are obtained by heating diphenylaniline and methylaniline with thionylaniline.

When thionylaniline (1 mol.) is heated with dimethylaniline (2 mols.) and some zinc chloride, *thiodimethylaniline*, $S(C_6H_4{\cdot}NMe_2)_2$, melting at 125°, is obtained, together with a *tetramethylphenyltriamidotriphenylmethane*, probably $NHPh{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, which crystallises from alcohol in nacreous leaflets, and melts at 176°; the

picrate melts at 185°. The colour *base* obtained on oxidation has all the properties of methyl violet.

Thionylmetachloraniline (*loc. cit.*) melts at 4°, and when dissolved in alcohol, together with metachloraniline and benzaldehyde, the *compound* $2C_6H_4Cl\cdot NH_2,SO_2,PhCHO$ separates with the development of heat; it forms white needles, and melts at 108°.

Thionylorthochloraniline boils at 207° (46 mm.), solidifies at −8°, is decomposed by water, and gives a *condensation derivative* with benzaldehyde.

Thionylparabromaniline crystallises from light petroleum in lustrous, yellow tables having an aromatic odour, and melts at 60—61°. *Thionylmetabromaniline* melts at 32°; and *thionylorthobromaniline* boils at 210° (46 mm.), and melts at 3—4°. Thionyltetrabromaniline, derived from Körner's tetrabromaniline (*Jahresb.*, 1875, 343) forms yellow needles, and melts at 78°.

Thionyliodaniline crystallises in yellowish-brown tables, melts at 54°, and gives a *condensation derivative*, $2C_6H_4I\cdot NH_2,SO_2,PhCHO$, with benzaldehyde melting at 121—122°. *Thionylmetadiiodaniline* melts at 74°, and its *condensation derivative* with benzaldehyde melts at 78°.

The *condensation derivative*, $2NO_2\cdot C_6H_4\cdot NH_2,SO_2,PhCHO$, derived from thionylmetanitraniline and benzaldehyde, forms small, yellow prisms, and melts at 90—91°. The corresponding *derivative* of thionylparanitraniline melts at 95—96°.

Thionylorthonitraniline forms small, yellow prisms, and melts at 52°; its *condensation derivative* with benzaldehyde melts at 88°.

The sp. gr. of thionylparatoluidine (*loc. cit.*) at 15° is 1·1685. *Thionylmetatoluidine* boils at 220°, and is more stable towards water than its isomeride. By heating thionylparatoluidine with aniline or diphenylamine at about 200°, condensation products are obtained.

Tetramethyltolyltriamidotriphenylmethane,

$$C_6H_4Me\cdot NH\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2,$$

melting at 177°, is obtained by heating together at 80° thionylparatoluidine (1 mol.), dimethylaniline (2 mols.), and zinc chloride; the *picrate* melts at 184°.

Thionylmetabromoparatoluidine forms small, yellowish-brown crystals, and melts at 47°; it is stable towards water. *Thionylmetabromorthotoluidine* crystallises in long prisms, and melts at 50°.

Thionylorthonitroparatoluidine melts at 44°; *thionylmetanitroparatoluidine* melts at 38—39°, and is very readily decomposed by water.

Thionylxylidine [$Me_2 : NSO = 1 : 3 : 4$], boils at 238°, does not solidify at −15°, and its sp. gr. is 1·149 at 14°. It yields with benzaldehyde the *condensation derivative*, $2C_6H_3Me_2\cdot NH_2,SO_2,PhCHO$, which melts at 98°, and on keeping is converted into xylidine sulphite and *benzylidenexylidine*, $C_6H_3Me_2\cdot N{:}CHPh$, an oil boiling above 300°. With anisaldehyde, a *compound* melting at 111° is obtained.

Thionylxylidine [$Me_2 : NSO = 1 : 2 : 4$] boils at 131° (20 mm.), and solidifies at −9°.

Thionylfluoro-xylidine [$Me_2 : F : NSO = 1 : 3 : 4 : ?$] is obtained

from a fluoro-xylidine which will be described in a subsequent paper; it boils at 142—144° (45 mm.).

Thionylxylidine [$Me_2 : NSO = 1 : 4 : 2$] boils at 119° (20 mm.), solidifies at −8°, and, when treated with benzaldehyde, yields the *benzylidenexylidine*, $C_6H_3Me_2{\cdot}N{:}CHPh$, melting at 96°.

Thionyl-ψ-cumidine boils under the ordinary pressure at 246°, but not without decomposition, and under a pressure of 20 mm. at 129°; it solidifies at −10°, is very stable towards water, and has a sp. gr. 1·078 at 14°. The *condensation product* with benzaldehyde,

$$2C_6H_2Me_3{\cdot}NH_2,SO_2,PhCHO,$$

melts at 108°, and an analogous *compound* with cinnamaldehyde melts at 68°.

Thionylcumidine, $C_6H_4Pr{\cdot}N{:}SO$, boils at 156—158° (60 mm.), and can be boiled with water for a considerable time without undergoing decomposition.

Thionylmesidine, $C_6H_2Me_3{\cdot}N{:}SO$, can be distilled in a current of steam without decomposition ensuing, boils at 241° with slight decomposition, has a sp. gr. 1·121 at 14°, and solidifies at −11°. The *condensation derivative* with benzaldehyde, $2C_6H_2Me_3{\cdot}NH_2,SO_2,PhCHO$, melts at 88°, and the corresponding *derivative* with anisaldehyde melts at 79·5°; when an alcoholic solution of the latter is exposed to the air, *methoxybenzylidenemesidine*, melting at 67°, is formed.

Thionylnitromesidine, derived from Noelting's nitromesidine (Abstr., 1891, 693), crystallises in groups of small, yellow needles, melts at 77°, and is slowly decomposed by cold water. Dinitromesidine (*loc. cit.*) yields a *thionyl derivative*, melting at 127°.

Unsuccessful attempts were made to isolate pure thionyl derivatives of para- and ortho-amidophenol. *Benzaldehydephenolparathionamic acid*, $OH{\cdot}C_6H_4{\cdot}NH_2,SO_2,PhCHO$, is prepared by saturating an alcoholic solution of paramidophenol with dry sulphurous anhydride, and adding the calculated quantity of benzaldehyde. It crystallises in colourless plates, and is insoluble in ether, but very soluble in water, and when heated loses the elements of sulphurous acid, and passes into benzylideneparamidophenol, $CHPh{:}N{\cdot}C_6H_4{\cdot}OH$. It therefore shows the melting point, 183°, of the latter compound. *Anisaldehydephenolparathionamic acid* forms white crystals; it becomes yellow at 140°, and melts at 188°, being converted into methoxybenzylideneparamidophenol.

Orthothionylanisidine, $OMe{\cdot}C_6H_4{\cdot}N{:}SO$, is an oil boiling at 203° (65 mm.). *Parathionylphenetidine*, $OEt{\cdot}C_6H_4{\cdot}N{:}SO$, boils at 220° (200 mm.), and solidifies to yellow needles when cooled; it melts at 32°.

Thionyl chloride converts metamidobenzoic acid into the anhydride (Harbordt, *Annalen*, **123**, 289); a thionyl derivative could not be prepared. *Ethylic metamidobenzoate* forms a *thionyl derivative*, $SO{:}N{\cdot}C_6H_4{\cdot}COOEt$, boiling at 195° (105 mm.); the corresponding *methylic* derivative boils at 212° (90—100 mm.), and melts at 57°.

Amidoazobenzene yields a *thionyl derivative*, $SO{:}N{\cdot}C_6H_4{\cdot}N_2Ph$, which crystallises in small, reddish-violet, lustrous needles, and melts at 113°; it cannot be distilled, even under diminished pressure, without decomposition.

Thionyldiamidoazobenzene (*thionylchrysoïdine*), $Ph{\cdot}N_2{\cdot}C_6H_3(NSO)_2$, forms red needles, and melts at 88°.

Thionyl-α-naphthylamine boils at 226° (100 mm.) and melts at 33°; the *condensation derivative* with α-naphthylamine and benzaldehyde, $2C_{10}H_7NH_2,SO_2,PhCHO$, melts at 84°, and the *condensation derivative* with aniline and benzaldehyde, $C_{10}H_7NH_2,PhNH_2,SO_2,Ph{\cdot}CHO$, melts at 103°.

Thionyl-β-naphthylamine melts at 53°, and the condensation product with β-naphthylamine and benzaldehyde melts at 112°; that with β-naphthylamine and anisaldehyde melts at 110°.

Thionylorthobromo-β-naphthylamine crystallises in long, yellow needles, melts at 118°, and with salicylaldehyde yields hydroxybenzylideneorthobromo-β-naphthylamine, $OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_{10}H_6Br$, melting at 144—145°.

The *thionyl derivative* of nitro-α-naphthylamine (m. p. 191°) melts at 89°; and the *thionyl derivative* of nitro-α-naphthylamine (m. p. 118—119°) melts at 134—135°.

Thionylmetaphenylenediamine melts at 44°, and is slowly decomposed by cold water. *Thionylparaphenylenediamine* melts at 115—116°, and is decomposed by hot water. Orthophenylenediamine and thionyl chloride interact, forming Hinsberg's piazthiole (Abstr., 1890, 161).

Thionylmetatoluylenediamine melts at 72—73°, and is readily decomposed by water. Orthotoluylenediamine interacts with thionyl chloride, forming methylpiazthiole (*loc. cit.*).

Thionylbenzidine (Abstr., 1891, 717) melts at 82°. *Thionyltolidine* forms reddish-violet needles, and melts at 90°. *Thionyldiamidostilbene*, $C_2H_2(C_6H_4{\cdot}N{:}SO)_2$, forms red needles, melts at 201—202°, and is fairly stable towards water. A. R. L.

Indene and Hydrindene. By A. Spilker (*Ber.*, **26**, 1538—1545). —It has already been shown by Krämer and Spilker (Abstr., 1891, 205) that hydrindene, when treated with sulphuric acid, behaves like a methylated benzene derivative, and yields sulphonic acids without formation of any resinous products. The further examination of the product has shown that it is a mixture of two monosulphonic acids, which must correspond in constitution with the α- and β-naphthalenesulphonic acids, as these are the only two possible forms. No definite proof has yet been obtained as to which is the α- and which the β-derivative, but from their general behaviour it appears probable that the acid formed in the larger quantity has the latter constitution.

β-Hydrindenesulphonic acid, $C_9H_9{\cdot}SO_3H$, is best obtained by the action of well-cooled sulphuric acid on hydrindene, and careful addition of a small quantity of water. The upper of the two layers which form is separated and mixed with more water, when it solidifies to a magma of crystals of β-hydrindenesulphonic acid, which contain water of crystallisation, and melt at 92°. The *sodium* salt crystallises in well developed prisms, which are very soluble in water and contain $4H_2O$, three of which are quickly given off in dry air. On treatment with phosphorus pentachloride, it yields a *sulphochloride*, $C_9H_9SO_2Cl$, which forms colourless, glassy crystals, melts at

45°, and is converted by ammonia into the corresponding *sulphonamide*, $C_9H_9SO_2NH_2$; the latter crystallises in narrow, satiny plates melting at 135·5—136° (corr.). *α-Hydrindenesulphonic acid* is always formed, together with the β-compound, the amount varying with the temperature at which the sulphonation is carried out; the acid and all its derivatives are more readily soluble than the corresponding β-compounds, and are only separated with difficulty from the latter. The separation is most readily effected with the sulphonamides, the *α-sulphonamide* being obtained in the form of white, nodular, crystalline aggregates melting at 91·5—92·5° (corr.).

In the previous paper, it was mentioned that indene, on treatment with bromine, gives a dibromide, and that this compound, on boiling with water, is converted into a substance supposed by Krämer and Spilker to be bromhydroxyhydrindene; this supposition has proved on further investigation to be correct, and the author has also been able to prepare *dichlorhydrindene*, $C_9H_8Cl_2$, and *chlorhydroxyhydrindene*, $C_9H_8Cl{\cdot}OH$, in a similar manner from indene, the latter compound crystallising in white, silky needles, and melting at 128—129°. Bromhydroxyhydrindene readily reacts with aqueous ammonia, forming *amidohydroxyhydrindene*, $OH{\cdot}C_9H_8{\cdot}NH_2$, and the corresponding *imidodihydroxydihydrindene*, $(OH{\cdot}C_9H_8)_2NH$. Cold water extracts the hydrobromide of the amido-compound, whilst the imido-base remains behind, and on purification crystallises in fascicular aggregates of white needles, or in long, narrow plates melting at 188·5° (corr.). It yields an *acetyl* derivative crystallising in hard, transparent, cube-shaped crystals, and melting at 220°, and an amorphous *nitroso*-compound. The amidohydroxyhydrindene is obtained from the hydrobromide by the action of alkalis, and crystallises from ether in white plates melting at 132—133°, which readily absorb moisture and carbonic anhydride from the air. The *hydrochloride* crystallises in satiny plates. When treated with nitrous acid, the amido-group is replaced by hydroxyl in the usual manner, yielding *hydrindene glycol*, $C_9H_8(OH)_2$, which may be crystallised from benzene, and then melts at 120°.

When indene is passed through an iron tube heated to bright redness, about 75 per cent. remains unaltered, and the remainder is converted almost entirely into hydrogen and chrysene. H. G. C.

2′.3′-Diphenylindoles. By A. Bischler and P. Fireman (*Ber.*, **26**, 1336—1349; compare Abstr., 1892, 1465).—Desyl bromide, $COPh{\cdot}CHPhBr$, like phenacyl bromide, is readily converted into indole derivatives by boiling with aromatic amido-compounds, the corresponding anilides being formed as intermediate products. *Desylanilide*, $COPh{\cdot}CHPh{\cdot}NHPh$, is readily obtained by boiling desyl bromide with aniline and a little alcohol, and crystallises in fascicular aggregates of yellow needles. Its *hydrochloride* forms a snow-white, crystalline mass which is decomposed by water, and the *acetyl* derivative crystallises in concentric groups of needles. *Desylparatoluidide*, $COPh{\cdot}CHPh{\cdot}NH{\cdot}C_6H_4Me$, obtained in a similar manner from desyl bromide and paratoluidine, crystallises from alcohol in deep yellow, fascicular aggregates of needles, and its *hydrochloride* forms a nacreous,

crystalline mass which is also decomposed by water; the *acetyl* derivative crystallises from alcohol in characteristic plates, and melts at 150°. *Desyl-β-naphthalide*, $COPh\cdot CHPh\cdot NH\cdot C_{10}H_7$, also crystallises in fascicular aggregates of needles, and melts at 131—132°; the *hydrochloride* crystallises in white needles.

2′.3′-Diphenylindole, $C_6H_4<^{CPh}_{NH}>CPh$, is obtained by boiling either desylanilide or desylparatoluidide with aniline; the product is fractionated in a vacuum, extracted with light petroleum, and recrystallised from alcohol; it then has the properties assigned to it by Fischer; its *picrate*, $C_{10}H_{15}N,C_6H_3N_3O_7$, forms pale-red needles, and melts at 154° with decomposition. 2′.3′-*Diphenylparatolindole*, $C_6H_3Me<^{CPh}_{NH}>CPh$, is prepared by boiling desylanilide or paratoluidide with paratoluidine, and crystallises in well-developed, fascicular aggregates of needles melting at 153°; its *picrate* forms chocolate-brown needles.

2′.3′-*Diphenylorthotolindole*, $C_6H_3Me<^{CPh}_{NH}>CPh$, obtained by substituting orthotoluidine for paratoluidine, crystallises in four-cornered plates or nodular aggregates of needles, melts at 128°, and forms a *picrate* which crystallises in coffee-brown needles melting at 173°. The solutions of all the above indoles show a blue fluorescence.

1′-*Methyl*-2′.3′-*diphenylindole*, $C_6H_4<^{CPh}_{NMe}>CPh$, is prepared by boiling desylanilide with methylaniline, and crystallises in concentric groups of nacreous needles melting at 139°; the *picrate* forms brownish-red needles, and melts at 158°. 2′.3′-*Diphenyl-β-naphthindole*, $C_{10}H_6<^{CPh}_{NH}>CPh$, is formed by boiling desyl-β-naphthalide with β-naphthylamine, and distilling the product under diminished pressure; it is separated with difficulty from the dinaphthylamine simultaneously formed, and crystallises in nodular aggregates of needles melting at 153—158°; it readily yields a *picrate* which forms flesh-coloured needles, and decomposes without melting at 155°.

Desylanilide is acted on by orthodiamines in quite a different manner to the monamines, derivatives of quinoxaline being formed; thus desylanilide and orthotoluylenediamine yield the diphenyltoluquinoxaline, $C_6H_3Me<^{N:CPh}_{N:CPh}$, already described by Hinsberg (*Annalen*, **237**, 327). H. G. C.

Dihydromethylketole. By E. Bamberger and H. Sternitzki (*Ber.*, **26**, 1291—1307).—Dihydromethylketole is converted by nitrous acid into the nitrosamine, $C_6H_4<^{CH_2\cdot}_{N(NO)}>CHMe$, which has been obtained in beautiful prisms belonging to the rhombic system, $a:b:c = 0{\cdot}4673:1:1{\cdot}5398$. When this compound, dissolved in dry ether, is treated with absolute alcoholic hydrogen chloride, it is converted into the isomeric *paranitrosodihydromethyl-*

ketole, $NO\cdot C_6H_3<\begin{matrix}CH_2\\NH\end{matrix}>CHMe$. This crystallises in small, yellow needles, melts at 103—105°, and yields pure green solutions. The *hydrochloride* forms small, yellowish-brown crystals, darkens at 160°, melts at 168° with decomposition, and when reduced with tin and hydrochloric acid, yields paramidodihydromethylketole (see this vol., i, 469).

Dinitrosodihydromethylketole, $NO\cdot C_6H_3<\begin{matrix}CH_2-\\N(NO)\end{matrix}>CHMe$, is obtained by adding sodium nitrite to an aqueous solution of the above hydrochloride. It crystallises in slender, moss-green needles, and melts at 105—106°.

Nitronitrosodihydromethylketole, $NO_2\cdot C_6H_3<\begin{matrix}CH_2-\\N(NO)\end{matrix}>CHMe$, is obtained by shaking the nitrosamine of the hydroketole with dilute nitric acid. It crystallises in lustrous leaflets, melts at 133·5°, and does not give the nitroso-reaction.

n-Methyldihydromethylketole, $C_6H_4<\begin{matrix}CH_2\\NMe\end{matrix}>CHMe$, is obtained by gradually adding methylic iodide to well-cooled hydromethylketole, and completing the reaction by heating on the water-bath. It is a colourless oil, boils at 222—225° under 722 mm. pressure, and is very similar to *n*-methyltetrahydroquinoline. The *methiodide* crystallises in beautiful, colourless prisms, and melts at 211°.

n-Dimethyldihydromethylketolium hydroxide,

$$C_6H_4<\begin{matrix}CH_2-\\NMe_2(OH)\end{matrix}>CHMe,$$

is obtained by shaking the preceding methiodide with silver hydroxide. It crystallises in long, lustrous needles, and decomposes at 100° to yield methyl alcohol and methyldihydromethylketole.

Nitro-n-methyldihydromethylketole, $NO_2\cdot C_6H_3<\begin{matrix}CH_2\\NMe\end{matrix}>CHMe$, is obtained by treating the tertiary base dissolved in sulphuric acid with potassium nitrate. It crystallises in dark red needles, melts at 48—49°, and is soluble in dilute mineral acids.

Dihydromethylketole condenses with ethylic acetoacetate and ethylic malonate in a similar way to tetrahydroquinoline, and yields compounds of the same type as juloline. The author proposes to name the simplest compound *liloline*. In the case of dihydromethylketole, a better yield of the condensation product is obtained with ethylic malonate than with ethylic acetoacetate, and also the intermediate bicyclic anilide has been isolated.

Ethylic dihydromethylketolyl-β-ketopropionate,

$$CH_2<\begin{matrix}CHMe\\C_6H_4-\end{matrix}>N\cdot CO\cdot CH_2\cdot COOEt,$$

is obtained by cautiously heating molecular proportions of dihydromethylketole and ethylic malonate on the sand-bath for seven hours. If the temperature is allowed to rise to 240—250°, a further action takes place, and the *lilolidine* is formed. It crystallises in long,

prismatic needles, melts at 209°, and in alcoholic solution gives a deep reddish-brown coloration with ferric chloride. It is easily soluble in alkalis, and is precipitated unchanged by acids. The aqueous solution of the sodium salt gives insoluble precipitates with many metallic salts. The *barium* salt forms small, transparent crystals.

α_1-Methyl-$\alpha\gamma$-diketolilolidine, $C_6H_3\begin{<}CH_2—CH_2\\CO\cdot CH_2\cdot CO\end{>}N$, is obtained by heating the preceding compound with concentrated hydrochloric acid at 150—160°. It crystallises in white, nacreous leaflets, melts at 298°, and is soluble in concentrated mineral acids and in alkalis. The sodium salt gives insoluble precipitates with salts of the heavy metals. The *hydrochloride* crystallises in long, colourless needles, and decomposes, on exposure to air, into hydrogen chloride and the free base. When treated with sodium nitrite in acetic acid solution, it yields a bluish-green dye, and a *nitroso-derivative* which crystallises in small, spherical aggregates, and melts at 151—152°.

Benzoyldihydromethylketole, when oxidised in alkaline solution with potassium permanganate, yields the following products:—Benzoylanthranilic acid, 56 per cent.; benzoic acid, 32 per cent.; acetylanthranilic acid, 1 per cent.; benzamide, 0·5 per cent.; a trace of methylketole, and a large quantity of oxalic acid.

Benzoyldihydromethylketole, $C_6H_4\begin{<}CH_2\\NBz\end{>}CHMe$, crystallises in beautiful, transparent prisms, and melts at 91·5°.

To determine the position of the nitroso-group in nitrosodihydromethylketole, the author has endeavoured to prepare paramidodihydromethylketole synthetically by converting paranitrophenylhydrazine into paranitrophenylhydrazoneacetone, and treating the latter with stannous chloride and then with reducing agents.

Paranitrophenylhydrazoneacetone crystallises in long, golden-yellow needles, and melts at 148—148·5°. When heated with stannous chloride, it yields a brown melt, and on subjecting this to steam distillation, a compound is obtained which crystallises in colourless needles, and melts at 61—62°. A nitromethylketole could not be isolated from the product. E. C. R.

Action of Phenylhydrazine on Lactones. By J. Ephraim (*Ber.*, **26**, 1376—1378; compare Meyer and Saul, this vol., i, 473).—When the unsaturated lactone benzalphthalide is heated with phenylhydrazine, condensation occurs, and a substance is obtained which crystallises in white needles melting at 171—172°, and is not affected by hydrochloric acid at 180°. It may also be obtained by heating deoxybenzoïnorthocarboxylic acid with phenylhydrazine in alcoholic solution, and is doubtless a derivative of phthalazone (this vol., i, 346), *3-phenyl-1-benzylphthalazone*, $CO\begin{<}C_6H_4\\N_2Ph\end{>}C\cdot CH_2Ph$.

C. F. B.

Phenylnaphthalenes and Zincke's Hydrocarbon $C_{16}H_{12}$. By R. Möhlau and R. Berger (*Ber.*, **26**, 1196—1200).—By the inter-

action of solid diazobenzene chloride and naphthalene in presence of aluminium chloride, α- and β-phenylnaphthalenes are formed, together with benzeneazonaphthalene and chlorobenzene; the product is treated with stannous chloride and hydrochloric acid, and, on purification and subsequent distillation, the phenylnaphthalenes are obtained in the fraction boiling above 260° under a pressure of 160 mm. The yield from 110 grams of aniline hydrochloride is 54·5 grams, nine-tenths of which consists of the α-derivative.

α-Phenylnaphthalene is separated from the β-compound by freezing; it is a pale yellow liquid with a faint blue fluorescence, boiling at 324—325°; on oxidation with potassium permanganate in acid solution, orthobenzoylbenzoic acid is formed.

β-Phenylnaphthalene crystallises from dilute alcohol in slender, lustrous plates, melts at 101—102°, and is volatile with steam; on oxidation with chromic anhydride in acetic acid solution, it is converted into a quinone, $C_{16}H_{10}O_2$ (m. p. 109—110°), which is identical with that obtained by Zincke and Breuer from the hydrocarbon formed by the interaction of phenyl glycol and phenylacetaldehyde.

J. B. T.

Essential Oil of Niaouli. By G. Bertrand (*Compt. rend.*, **116**, 1070—1073).—Essential oil of niaouli, obtained from *Melaleuca viridiflora*, a tree which grows abundantly in New Caledonia, is a pale yellow oil with a greenish tinge, and a sweet odour resembling that of oil of cajeput. It is prepared by distilling the leaves with water, the yield being 2·5 per cent. of the weight of the leaves. It is somewhat viscous and is dextrogyrate; sp. gr. at 12° = 0·922.

Essential oil of niaouli contains minute quantities of valeric acid, ethylic valerate, benzaldehyde, and amyl alcohol. It consists chiefly of a terebenthene boiling at 155—156° and a liquid boiling at 173—175°. The terebenthene is a mobile liquid with the usual odour of terebenthene; sp. gr. at 12° = 0·865; specific rotatory power $[\alpha]_D = +36°\ 3'$. It yields a crystalline hydrochloride which in alcoholic solution has a specific rotatory power $[\alpha]_D$ +25° 9′.

The fraction boiling at 173—175° when cooled to −6° yields crystals of an eucalyptol, which melts at 1° and boils at 175°; sp. gr. at 12° = 0·930; vapour density = 5·28. When treated with dry hydrogen chloride at −10°, it yields a crystalline, unstable compound, $2C_{10}H_{18}O,HCl$, which is immediately decomposed by water with separation of eucalyptol. The portion remaining liquid at −6° is a mixture of the eucalyptol with a citrene having a lævorotatory power of about −20°.

The smaller fraction of the original oil boiling above 180° consists of a terpilenol having a lævorotatory power of $[\alpha]_D = -2°\ 10'$.

It is noteworthy that, leaving aside the terebenthene, oil of niaouli contains eucalyptol, a citrene, and a terpilenol, and in this respect resembles the terpinol obtained by List by the action of dilute acids on the terpin resulting from the spontaneous hydration of terpenes.

C. H. B.

Liquid Isomeride of Hydrocamphene. By L. Bouveault (*Compt. rend.*, **116**, 1067—1070).—The product obtained by the action of dry hydrogen chloride on oil of turpentine was heated to

boiling and gradually mixed with sufficient sodium to remove the whole of the chlorine, and the product was repeatedly fractionated, the hydrocamphene being removed by repeated cooling and crystallisation. A fraction was thus obtained boiling at 148—151° and yielding no crystals when cooled; its composition corresponded with a mixture of 75 parts of a hydrocarbon $C_{10}H_{18}$ and 25 parts of a hydrocarbon $C_{10}H_{16}$. Treatment of this fraction with hydrogen chloride does not remove the whole of the terpene, but this is readily effected by treatment with bromine in chloroform solution, and on fractionating the product, a colourless liquid boiling at 148—149° is obtained. It has the composition $C_{10}H_{18}$, and its vapour density corresponds with the molecular weight 138. This liquid, which has a faint odour of oranges, is isomeric with hydrocamphene, from which it is readily distinguished by its boiling point and the fact that it does not crystallise. It seems also to be isomeric with the camphene hydride obtained by Berthelot by the action of hydrogen iodide on oil of turpentine.

The new hydrocarbon is not attacked by bromine or by fuming sulphuric acid at the ordinary temperature. The author calls it provisionally *hydropinene*. C. H. B.

Action of Zinc on Chlorocamphor: Relation between Camphor and Carvacrol. By A. Étard (*Compt. rend.*, **116**, 1136—1139).—When monochlorocamphor mixed with about 10 per cent. of zinc chloride is boiled without distillation until evolution of hydrogen chloride ceases and is then distilled, carvacrol is obtained in quantity corresponding with 65 per cent. of the calculated yield. At the same time some carbonic oxide is evolved and a hydrocarbon C_8H_{16} is formed. It boils at 137°; sp. gr. at 15° = 0·795; index of refraction $[n]_D = 1{\cdot}434$, $R = \frac{n^2 - {}_1M}{n_2 - {}_2d} = 40{\cdot}58$. The value calculated on the assumption that there are no double bonds is 39·32. This hydrocarbon seems to be identical with the campholene of de Lalande, Kachler, and Zürrer. It would follow, therefore, that the benzene ring has been broken and the campholene corresponds with the camphorone that yields α-methylglutaric acid on oxidation. The hydrocarbon C_8H_{14}, from which campholene is supposed to be derived, cannot be a tetrahydro-xylene, for it is derived from camphoric anhydride or copper camphorate with loss of carbonic anhydride.

Chlorocamphor seems to behave as a hydrochloride of carvacrol and in this respect is strictly analogous to carvol hydrochloride. It follows that camphor may be regarded as a hydrocarvacrol, and the fact that it does not dissolve in alkalis is not surprising in view of the fact that the phenolic function of carvacrol itself is very weak and is necessarily diminished by hydrogenation. C. H. B.

Camphoric acid Derivatives. By H. Rupe and C. Maull (*Ber.*, **26**, 1200—1202).—Bromocamphoric anhydride is readily prepared according to Volhard's method by the action of bromine and phosphorus on camphoric anhydride; it easily reacts with certain bases,

crystalline compounds of the type $NHR{\cdot}C_8H_{13}C_2O_3$ have been obtained with aniline, paratoluidine, phenylhydrazine, and piperidine. The *anilidoanhydride* melts at 123° and on hydrolysis with soda, yields the corresponding *acid*, which melts at 154°.

By the action of hydrochloric acid on the anilidoanhydride, hydroxycamphoric acid lactone (camphanic acid), $COOH{\cdot}C_8H_{13}{<}\begin{matrix}O\\|\\CO\end{matrix}$, is formed.

On treatment of bromocamphoric lactone with zinc-dust and acetic acid, camphoric acid is regenerated.

The formation of tetrahydro-xylene from water and camphanic acid, as observed by Wreden, cannot be confirmed; a mixture of lauronolic acid and camphoric lactone, which boils at 210°, appears to be the only product.

Tetrahydro-xylene is obtained by the distillation of calcium camphanate; it boils at 118—122°, and instantaneously decolorises potassium permanganate and bromine water. J. B. T.

Camphoric acid. By K. Auwers and H. Schnell (*Ber.*, **26**, 1517—1532).—The action of bases on bromocamphoric anhydride does not take place, according to the authors, in correspondence with the equation

$$C_8H_{13}Br{<}\begin{matrix}CO\\CO\end{matrix}{>}O + 2NH_2R = NHR{\cdot}C_8H_{13}{<}\begin{matrix}CO\\CO\end{matrix}{>}O + NH_2R{\cdot}HBr,$$

as Rupe and Maull (preceding abstract) assert, but rather with the equations

$$C_8H_{13}Br{<}\begin{matrix}CO\\CO\end{matrix}{>}O + 2NH_2R = NHR{\cdot}CO{\cdot}C_8H_{13}Br{\cdot}COOH$$

$$+ NH_2R = NHR{\cdot}CO{\cdot}C_8H_{13}{<}\begin{matrix}CO\\|\\O\end{matrix} + NH_3RBr.$$

Thus what Rupe and Maull supposed to be anilidocamphoric anhydride is the anilide of camphanic acid. The chief evidence in favour of this view is that the acid obtained from such a compound by the action of soda is monobasic, not bibasic.

Camphoramic acid, $NH_2{\cdot}CO{\cdot}C_8H_{14}{\cdot}COOH$, prepared from camphoric anhydride and aqueous ammonia, melts at 174—175°, and, when pure, easily gives off ammonia on boiling with dilute soda (compare Claisen and Manasse, this vol., i, 479).

Camphormethylamic acid, $NHMe{\cdot}CO{\cdot}C_8H_{14}{\cdot}COOH$, obtained from camphoric anhydride and 33 per cent. methylamine solution, when recrystallised from aqueous acetone, forms rhombic prisms, and melts at 225°. It is a monobasic acid easily soluble in hot water.

Camphordimethylamic acid, $NMe_2{\cdot}CO{\cdot}C_8H_{14}{\cdot}COOH$, forms long, pointed prisms, and melts at 186—187°. It dissolves with decomposition in hot water.

Bromocamphoric anhydride, when heated with water, yields camphanic acid, and, when warmed for two hours on the water-bath

with aqueous alcohol containing a little potassium cyanide, gives *ethylic camphanate*. This salt melts at 62° and boils at 195—196°.

Camphanamide is formed when dry ammonia is led into a solution of bromocamphoric anhydride in boiling chloroform. It may also be produced by acting, at the ordinary temperature, on ethylic camphanate with aqueous ammonia. It melts at 208°, is easily soluble in water, alcohol, hot benzene, and chloroform, and insoluble in light petroleum. By heating with 10 per cent. potash solution, it may be converted into *hydroxycamphoramic acid*, $NH_2{\cdot}CO{\cdot}C_8H_{13}(OH){\cdot}COOH$, melting at 155—156°. The calcium salt crystallises with 2 mols. of water.

Camphanmethylamide is the product of the interaction of bromocamphoric anhydride and methylamine solution, much heat being evolved on its formation. It melts at 133°, and is soluble in water, and organic solvents except light petroleum. It is easily converted by dilute potash solution into the potassium salt of *hydroxycamphormethylamic acid*, $NHMe{\cdot}CO{\cdot}C_8H_{13}(OH){\cdot}COOH$, which melts at 156° with decomposition.

Camphananilide is formed in boiling chloroform solution from aniline and bromocamphoric anhydride. It melts at 126°, is insoluble in water, but soluble in alcohol, ether, chloroform, and benzene. It is transformed into *hydroxycamphoranilic acid* by heating in alcoholic solution with slight excess of potash, and acidifying. This acid melts at 151° and passes easily into camphananilide.

Camphanphenylhydrazide is obtained in the same way as the anilide. It forms white, silky needles melting at 193°. J. W.

Bromal Borneolates. By J. Minguin (*Compt. rend.*, **116**, 889—891).—Bromal combines readily with the various modifications of borneol, forming products which can be crystallised from toluene. The borneolates formed have the composition $CBr_3{\cdot}CH(OH){\cdot}OC_{10}H_{17}$. That derived from racemic borneol crystallises well only from light petroleum. The products from the borneols have the following melting points and molecular rotatory powers when dissolved in toluene.

	M. p.	Rotatory power.
Dextrogyrate borneol	105—109°	$[\alpha]_D = +52{\cdot}4°$
Lævogyrate ,, ...	105—109	$[\alpha]_D = -52{\cdot}4$
Racemic ,, ...	79— 82	$[\alpha]_D = 0$

The inactive borneol ($\alpha\beta$-) yields a viscous, non-crystallisable liquid, with a rotatory power $[\alpha]_D = -3{\cdot}4°$.

Combination of bromal with the isocamphols takes place somewhat less readily, but the products are similar. C. H. B.

New Isomerides of Santonin and Santonous acid. By A. Andreocci (*Ber.*, **26**, 1373—1376).—When santonin is dissolved in fuming hydrochloric acid, and the solution allowed to remain in a cool place, *desmotroposantonin* crystallises out. This substance is isomeric with santonin, and has the constitution

$$\begin{matrix} HC{\cdot}CMe{\cdot}C{\cdot}CH_2{\cdot}CH & \text{——} & O \\ | & & \\ OH{\cdot}C{\cdot}CMe{\cdot}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe \end{matrix} > CO,$$

the $CH_3{\cdot}CO$ group of santonin having been doubtless converted into $CH{:}C(OH)$. It forms small, white needles, melts at 260° when quickly heated, and has specific rotation +112°. It has lost the ketonic properties of santonin, but has acquired phenolic properties, for it yields an *acetyl derivative*, melting at 156°. It retains the lactonic properties of santonin. When reduced with zinc and acetic acid, it yields *desmotroposantonous acid* (*dimethylhydroxytetrahydronaphthylpropionic acid*), $C_{15}H_{20}O_3$, which melts at 175°, has the specific rotation −53·3°, is converted, by fusion with potash into propionic acid and dimethylnaphthol ($Me_2 : OH = 1 : 4 : 3$), and is isomeric with santonous acid. C. F. B.

Dihydroxypyridines. By S. Ruhemann (*Ber.*, **26**, 1559—1561; compare Trans., 1893, 259, 874).—The author points out the strong analogy which exists between the $\alpha x'$-dihydroxypyridines and resorcinol; the former yield, with phthalic anhydride, phthaleïns having a red odour and blue fluorescence, and give, with ferric chloride in aqueous solution, yellow colouring matters, which are probably hydroxyquinones. Resorcinol and its derivatives yield colouring matters when oxidised in ammoniacal solution, and the dihydroxypyridines behave in a similar manner; the colouring matters formed have a cantharidin lustre, and dissolve in alcohol with a bluish colour, and in acetic acid with reddish-violet colour. They are at present undergoing further investigation.

Bromine acts on dihydroxypyridines, with formation of substitution products; thus, methyldihydroxypyridine yields a *dibromo*-derivative, $C_6H_3Br_2NO_2$, which crystallises in yellow needles, and melts with decomposition at 145°. It is not affected by warm water or cold dilute potash, but decomposes on boiling with either water or alkalis. H. G. C.

Action of Chloral on Pyridine Bases from Messel. By A. Einhorn and A. W. Gilbody (*Ber.*, **26**, 1414—1422).—A mixture of pyridine bases, obtained in distilling the bituminous shale of Messel, near Darmstadt, was separated into two portions, boiling respectively below 137° and from 137° to 160°, and these portions were treated separately with chloral, as described in Abstr., 1892, 75. From the first, the compound of chloral with 2-picoline was isolated; from the second, a compound with 2 : 6-lutidine, hitherto unknown.

2 : 6-*Picolyl-ω-trichloro-α-hydroxypropane* (2 : 6-*lutidine chloral*), $C_5NH_3Me{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, forms small, lustrous tables melting at 105·5°. The *hydrochloride* (+ H_2O) crystallises in cubes, melting at 134°; the *hydrobromide* in small plates, melting at 113·5°; the *platinochloride* in orange-coloured plates, melting with decomposition at 210°; and the *aurochloride* in yellow, transparent needles, melting at 165°. When the hydrochloride is boiled with alcoholic potash in excess, 2 : 6-*picolylacrylic acid*, $C_5NH_3Me{\cdot}CH{:}CH{\cdot}COOH$, is obtained; it forms rhombic tables, melting at 169·5°; the *hydrochloride* crystallises in small plates, melting at 234°; and the *platinochloride* in lustrous, yellow crystals, melting with decomposition at 231°; metallic salts may also be prepared. If, instead of alcoholic potash, aqueous sodium carbonate is used, then 2 : 6-*picolyl-α-hydroxypropionic* (2 : 6-*picolyl-*

lactic) *acid*, $C_5NH_3Me{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$, is obtained, and may be isolated by means of the copper salt; it forms tiny, quadrangular crystals, melting at 166°. The *platinochloride* forms orange-red crystals, melting at 185°; the *aurochloride* (+ H_2O) yellow tables, melting at 100°, when anhydrous at 143—144°. The normal *copper salt* is blue, and, when recrystallised from boiling water, is partially decomposed into the green basic salt,

$$(C_5NH_3Me{\cdot}CH_2{\cdot}CH(OH){\cdot}COO)_2Cu,CuO + 1\tfrac{1}{2}H_2O.$$

C. F. B.

Tetrahydroisoquinoline. By E. Bamberger and W. Dieckmann (*Ber.*, **26**, 1205—1221).—In spite of the close similarity of quinoline and isoquinoline in properties, the tetrahydro-derivatives of these compounds should exhibit considerable differences, since tetrahydroquinoline, $C_6H_4<\begin{matrix}CH_2{\cdot}CH_2\\ NH{\cdot}CH_2\end{matrix}$, may be regarded as an alkylaniline, but tetrahydroisoquinoline, $C_6H_4<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}NH\end{matrix}$, as a benzylamine base, closely related to piperidine; this proves to be correct, as the latter has an alkaline reaction, readily combines with carbonic anhydride and carbon bisulphide, and with diazo-compounds yields diazoamido-derivatives. The preparation of tetrahydroisoquinoline from commercial isoquinoline containing 60 per cent. of quinoline is described. The following reactions, in addition to those already known, serve to characterise the base; potassium dichromate does not give either a precipitate or a coloration; bromine water gives a yellow, oily precipitate; potassium ferrocyanide produces a colourless salt, crystallising in needles; with benzoquinone, a red coloration is obtained, changing to carmine on warming; calcium hypochlorite gives an oily chlorimide, the alcoholic solution of which produces, with aniline and hydrochloric acid, a green colour, changing to violet-red on warming. The *mercurochloride* is crystalline, and melts at 151°; the *picrate* crystallises in lustrous, yellow needles melting at 195°.

The authors remark that the hydroquinolines also give characteristic colours with quinone, tetrahydroquinoline yielding a deep violet-blue coloration.

Diazoamidobenzenetetrahydroisoquinoline, $C_9NH_{10}{\cdot}N_2Ph$, is prepared by the action of diazobenzene nitrate or chloride on tetrahydroisoquinoline in presence of sodium acetate, and crystallises from light petroleum in colourless, long, prismatic plates, melting at 61·5°. The compound exhibits all the properties of the diazoamido-derivatives, gives a red coloration with molten resorcinol, a violet-red colour with glacial acetic acid and α-naphthylamine, whilst, on heating with acids, the original base is regenerated, together with phenol and nitrogen; it does not explode when heated. The *picrate* crystallises in needles.

Nitrosotetrahydroisoquinoline, $C_9NH_{10}{\cdot}NO$, is formed by heating the tetrahydro-base with sodium nitrite and dilute hydrochloric acid, and crystallises from light petroleum in slightly coloured, strongly refractive, flat needles, melting at 53°; it is soluble in concentrated hydrochloric acid, from which it is precipitated unchanged on dilution.

Tetrahydroisoquinoline tetrahydroisoquinoyldithiocarbamate, $C_9NH_{10}\cdot CSSH,C_9NH_{11}$, crystallises from alcohol in colourless needles, which, after previous softening, melt at 173—174° with decomposition. The *copper salt* is reddish-brown and amorphous; the *lead salt* is colourless and amorphous; the *mercuric salt* is crystalline; the *silver salt* pale yellow, turning black on warming.

Tetrahydroisoquinoylcarbamide, $C_9NH_{10}\cdot CONH_2$, crystallises in colourless, lustrous plates, melting at 169°.

Phenyltetrahydroisoquinoylcarbamide, $C_9NH_{10}\cdot CO\cdot NHPh$, is deposited from alcohol in stellate groups of slender needles, melting at 144°.

Phenyltetrahydroisoquinoylthiocarbamide, $C_9NH_{10}\cdot CS\cdot NHPh$, crystallises from alcohol in slender, lustrous needles, and melts at 140°. Attempts to methylate the tetrahydro-base were unsuccessful; by the action of methylic iodide, the quaternary iodide is formed, and is deposited from alcohol in lustrous needles or plates melting at 189°.

Acetyltetrahydroisoquinoline is crystalline, melts at 46°, and boils at 220—225° under a pressure of 70 mm. The *benzoyl derivative* forms highly refractive, rhombic crystals, melts at 129°, and boils with decomposition at 245—250° under a pressure of about 50 mm.

Benzoyltetrahydroisoquinoline, on oxidation with potassium permanganate in alkaline solution, yields *ortho-ω-benzoylamidoethylbenzoic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHBz$, which closely resembles benzoylamidovaleric acid and benzoylhomoconiic acid from piperidine and coniine respectively; the acid is insoluble in benzene and light petroleum, and crystallises from water or ethylic acetate in clusters of silky, lustrous needles or prisms, which melt at 172°; it is soluble in concentrated hydrochloric acid, is reprecipitated on dilution, and appears to be without physiological action. The yield is 50—60 per cent., benzoic acid (15 per cent.), benzamide (6 per cent.), phthalic acid (20 per cent.), and traces of oxalic acid being also formed, together with a ketonic acid, which could not be isolated. The salts of the heavy metals are almost all extremely sparingly soluble; the *silver salt* is crystalline and stable towards light; the *lead salt* is amorphous and soluble in chloroform or alcohol; the *copper*, *barium*, and *calcium salts* crystallise in small, lustrous plates.

Benzoylhydroisocarbostyril, $C_6H_4<\begin{matrix}CO\cdot NBz\\ CH_2\cdot CH_2\end{matrix}$, is prepared by heating the acid with acetic anhydride, and crystallises from alcohol in long, lustrous prisms and in slender needles melting at 132°; the compound is hydrolysed by soda, with formation of benzoic acid and hydroisocarbostyril (see below).

Amidoethylbenzoic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$, is obtained, together with benzoic acid and hydroisocarbostyril (see below), by heating benzoylamidoethylbenzoic acid with concentrated hydrochloric acid in a sealed tube at 150—160°; after purification and treatment of the hydrochloride with silver oxide in alcoholic solution, the acid crystallises in small, lustrous, highly refractive needles, which melt at 160—165°. The *salts* formed both with mineral acids and

heavy metals are readily soluble in water. The yield is 30 per cent. of the benzoylamido-acid employed, together with an equal quantity of hydroisocarbostyril. The *hydrochloride* crystallises from alcohol in colourless plates melting at 199—200°. The *platinochloride* is deposited from water in slender, yellow needles, which melt at 230° with decomposition.

Hydroisocarbostyril, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CH_2\cdot CH_2\end{matrix}$ (*dihydroisoquinolone*), is formed by heating benzoylhydroisocarbostyril with soda; by heating the benzoyl-acid with hydrochloric acid (see above); by the evaporation of the amido-acid or the hydrochloride in aqueous solution, or by heating the amido-acid above its melting point; it is most readily prepared by distillation of the benzoyl-acid, benzoic acid and a little benzonitrile being also formed; it crystallises from light petroleum in groups of lustrous needles, melts at 70—71°, and boils above 300° without decomposition. The compound closely resembles the alkaloïds; it produces dilation of the pupil, gives white, flocculent precipitates with phosphomolybdic acid and with phosphotungstic acid, which crystallise from water; with solutions of iodine in potassium iodide and of potassium bismuthiodide, reddish-brown precipitates are produced; it is unaffected by heating with moderately concentrated hydrochloric acid, and is scarcely acted on by 10 per cent. potash. Attempts to prepare a methyl derivative were unsuccessful, and it could not be converted into isocarbostyril, nor could the latter compound be reduced to the quinolone. The *acetyl derivative*,

$$C_6H_4<\begin{matrix}CO\cdot NAc\\ |\\ CH_2\cdot CH_2\end{matrix},$$

is deposited from dilute alcohol in lustrous crystals, which melt at 100°. J. B. T.

Phenometadiazine Derivatives. By A. Bischler and E. Burkart (*Ber.*, **26**, 1349—1353; compare Abstr., 1891, 745; this vol., i, 47).—In addition to the phenometadiazines already prepared by Bischler's method, the authors have prepared two oxyphenometadiazines by the action of ammonia on acidyl-orthamidobenzoic acids. Thus, when the ammonium salt of formylorthamidobenzoic acid is heated, it loses water and is converted into 4′-oxyphenometadiazine $C_6H_4<\begin{matrix}N=CH\\ |\\ CO\cdot NH\end{matrix}$, which has been prepared in a different manner by Weddige. The acetyl derivative of orthamidobenzoic acid gives the methyl derivative of this compound, which has also been described by Weddige. When acetylorthamidoacetophenone is heated with ammonia, it yields 2′ : 4′-dimethylphenometadiazine, $C_6H_4<\begin{matrix}N=CMe\\ |\\ CMe:N\end{matrix}$; the latter is a thick, yellow oil, with a deep yellowish-green fluorescence, which boils at 249° under a pressure of 713 mm., and readily combines with $2H_2O$, to form a crystalline hydrate; the latter forms snow-white, satiny, felted needles, melts at 72°, and loses water over sulphuric acid or on warming. Its *picrate*, $C_{10}H_{10}N_2,C_6H_3N_3O_7$, forms

yellowish, crystalline crusts, and melts at 170° with complete decomposition.

In order to obtain the corresponding methylphenometadiazine, the author endeavoured to prepare the corresponding formylorthamidoacetophenone by heating the amidoketone with formic acid. The resulting product has, however, the formula $C_6H_4<\begin{matrix}CMe{:}CH\\ |\\ N=C\cdot C_6H_4\cdot NH_2\end{matrix}$, and is formed by the condensation of 2 mols. of the amidoketone with elimination of water; the amido-group is then acted on by the excess of formic acid with formation of the formyl derivative. The first compound is isomeric with flavaniline, and may therefore be termed *isoflavaniline*. The formyl derivative crystallises from alcohol in short, chamois yellow needles, and melts at 107°; it is dissolved by concentrated hydrochloric acid, and, on warming, isoflavaniline hydrochloride separates as a pink powder which decomposes on heating without melting. Its solutions have a deep yellow colour.

H. G. C.

Phenometadiazine Derivatives. By A. Bischler and F. J. Howell (*Ber.*, **26**, 1384—1399; compare Abstr., 1891, 745, this vol., i, 47, and preceding abstract).—2′:4′-Dimethylphenometadiazine (preceding abstract) is a colourless oil which boils at 249°, and has sp. gr. 1·0980 at 16°. The *hydrochloride* (+ 1HCl) is a white powder. When reduced with sodium in hot amyl alcoholic solution, it yields *tetrahydrodimethylphenometadiazine*, $C_{10}H_{14}N_2$, which was obtained in an impure state as a dark-coloured oil which boiled at 235—242°, had sp. gr. 1·0981 at 16°, gave Liebermann's nitroso-reaction, and yielded a *dibenzoyl* derivative, as large, colourless prisms melting at 155°, and a *diacetyl* derivative as small, silky needles melting at 110°.

Propionamidoacetophenone forms large plates melting at 68°. *4′-Methyl-2′-ethylphenometadiazine*, $C_6H_4<\begin{matrix}N=C\,Et\\ |\\ CMe{:}N\end{matrix}$, is a colourless oil which boils at 259—260°, has sp. gr. 1·0723 at 16°, and solidifies when allowed to remain over sulphuric acid; the *hydrochloride* forms a white, deliquescent mass; the *picrate* a yellow, crystalline powder.

Butyramidoacetophenone forms colourless prisms, melting at 52°. *4′-Methyl-2′-propylphenometadiazine* forms a colourless oil which boils at 269—270°, and has sp. gr. = 1·0546 at 16°; the *picrate* forms a yellow, the *platinochloride* a reddish-yellow, and the *hydrochloride* a deliquescent, white, powder.

Isobutyramidoacetophenone forms large prisms melting at 50°. *4′-Methyl-2′-isopropylphenometadiazine* is a colourless oil which boils at 268—269°, has sp. gr. 1·0556 at 16°, and solidifies partially on standing; the *platinochloride* forms a reddish-yellow, the *picrate* a bright-yellow, powder.

Benzamidoacetophenone forms small needles melting at 98°. *4′-Methyl-2′-phenylphenometadiazine* melts at 90°, and forms stellate clusters of white needles; the *picrate* forms a bright-yellow, the *hydrochloride* a white, mass.

Phenylacetamidoacetophenone forms colourless prisms melting at 79°. *4'-Methyl-2'-benzylphenometadiazine* melts at 76°, and forms colourless needles or plates.

Cinnamylamidoacetophenone, $COMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh$, forms large, rhombic tables melting at 91°. *4'-Methyl-2'-phenylethenylphenometadiazine* forms colourless needles melting at 96°, and yields an unstable *dibromide*. The *hydrochloride* and picrate form yellow, crystalline powders.

Chloracetamidoacetophenone forms white needles melting at 81°. When heated with ammonia, it yields a mixture of different phenometadiazines; probably it first forms monochlorodimethylphenometadiazine, and the chlorine atom in this reacts with excess of ammonia yielding primary, secondary, and tertiary amines.

Trichloracetamidoacetophenone crystallises in needles.

Oxidation of Phenometadiazines.—Phenometadiazines are not readily oxidised by chromic acid or permanganate. With the former, 4'-methyl-2'-phenylphenometadiazine yields a little 2'-phenylphenometadiazine; by the latter dibenzoyltetrahydrodimethylphenometadiazine is oxidised to oxalic and benzoic acids.

Synthesis of Quinoline Derivatives.—In the mother liquor from 4'-methyl-2'-benzylphenometadiazine was contained a *phenylmethyloxyquinoline*, $C_6H_4<\begin{matrix}NH—CO\\ CMe:CPh\end{matrix}$, which had been doubtless formed by direct condensation, without participation of ammonia, of the phenylacetamidoacetophenone, from which it can also be obtained by the action of cold alcoholic potash. It forms long, silky needles melting at 275°. In a similar manner there was obtained from acetamidoacetophenone a small quantity of a methyloxyquinoline, melting at 221°, identical with the oxylepidine prepared by Knorr from acetacetanilide. C. F. B.

Oxazolines and Thiazolines. By A. Salomon (*Ber.*, **26**, 1321—1330).—*Bromethylorthotoluamide*, $CH_2Br{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4Me$, is obtained by shaking bromethylamine hydrobromide with aqueous sodium hydroxide and orthotoluic chloride. It crystallises in lustrous scales, melts at 70—71°, and is not very stable.

μ-Orthotolyloxazoline, $\begin{matrix}CH_2{\cdot}O\\ |\\ CH_2{\cdot}N\end{matrix}>C{\cdot}C_6H_4Me$, is obtained by treating the preceding compound with an alkali. It boils at 254—255° under 755·5 mm. pressure, and is volatile with steam. The *picrate* crystallises in yellow needles, and melts at 144—145°. The *platinochloride* melts at 188—189° with decomposition.

Amidoethylic orthotoluate, $C_6H_4Me{\cdot}COO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, is obtained by treating the above oxazoline with a molecular proportion of acid; it is a colourless oil. The *hydrobromide* crystallises in colourless tablets, and melts at 155—156°. The *picrate* melts at 187—188°.

Chlorethylorthotoluamide, $C_2H_4Cl{\cdot}NH{\cdot}CO{\cdot}C_7H_7$, is obtained by heating the oxazoline with excess of hydrochloric acid on the water-bath. It crystallises in white needles, and melts at 72—73°.

β-Bromopropylorthotoluamide, $CHMeBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_7H_7$, ob-

tained in a similar way to the bromethyl compound, crystallises in colourless needles, and melts at 85—86°.

β-Methylorthothotolyloxazoline, $\begin{matrix}CHMe\cdot O\\ |\\ CH_2-N\end{matrix}\!\!>C\cdot C_7H_7$, is obtained by heating the preceding compound with alcoholic potash on the water-bath. It is a colourless oil, and boils at 257—258° under 763 mm. pressure. The *picrate* crystallises in yellow needles, and melts at 128—129°. The *platinochloride* crystallises in rhombic leaflets, and melts at 180—181°. When treated with excess of hydrochloric acid, it yields β-chloropropylorthotoluamide, which crystallises in white needles, and melts at 84°.

β-Amidopropylic orthotoluate hydrobromide is obtained by evaporating an aqueous solution of bromopropyltoluamide. It crystallises in white needles, and melts at 139—140°. The *free base*,

$$C_7H_7\cdot COO\cdot CHMe\cdot CH_2\cdot NH_2,$$

is easily soluble in water. The *picrate* crystallises in yellow plates, and melts at 191—192°. The *platinochloride* melts at 213—214° with decomposition.

Bromethylparatoluamide, prepared in the same way as the ortho-compound, crystallises in white leaflets, melts at 128—129°, and is very unstable.

β-Paratolyloxazoline crystallises in beautiful white needles, melts at 66°, boils at 264—265° under 700·2 mm. pressure, and is volatile with steam. The *picrate* melts at 187—188°. The *platinochloride* crystallises in orange needles, and melts at 185—186° with decomposition. When evaporated with fuming hydrochloric acid, it yields chlorethylparatoluamide.

Amidoethylic paratoluate hydrobromide is obtained by evaporating bromethylparatoluamide with water. It crystallises in rhombic tablets, and melts at 167°. The *picrate* crystallises in yellow needles, and melts at 179—180°.

β-Bromopropylparatoluamide is very unstable and easily goes over into the oxazoline. It crystallises from light petroleum in needles, begins to melt at 74°, then solidifies, and melts again at 157—158°.

β-Methylparatolyloxazoline is an oil, and boils at 264—265° under 754° mm. pressure. The *picrate* melts at 182—183°. The *platinochloride* crystallises in flat, orange leaflets, and melts at 183—184° with decomposition. When evaporated with fuming hydrochloric acid, it yields β-chloropropylparatoluamide, which crystallises in white needles, and melts at 77—78°.

Thiazolines are obtained by heating molecular proportions of phosphorus pentasulphide and the acidyl derivatives of brominated amines at 150° in an oil-bath.

β-Methylorthotolylthiazoline is an oil which boils at 284—295° under 753·5 mm. pressure; it is volatile with steam, and has an odour resembling that of quinoline. The *picrate* crystallises in yellow needles, and melts at 135—136°.

β-Methylparatolylthiazoline is a pale-yellow oil, and distils at 294—295° under 757·5 mm. pressure. The picrate crystallises in

yellow needles and melts at 140—141°. The *platinochloride* melts at 175—176° with decomposition.

The author has also prepared methyl-μ-phenylthiazoline, ortho- and para-tolylthiazoline, which have been previously described by Gabriel and Heymann (Abstr., 1891, 701). Methyl-μ-phenylthiazoline picrate prepared by this method melts at 156—157°; when prepared by Gabriel's method, it melts at 154°. Orthotolylthiazoline, contrary to the statement of Gabriel and Heymann, distils without decomposition at 281—282° under 760·5 mm. pressure. E. C. R.

Paranitrophenylmethyloxybiazolone and its Decomposition Products. By M. Freund and H. Haase (*Ber.*, **26**, 1315—1321).—Phenylmethyloxybiazolone yields a mono- and a di-nitro-derivative. The mononitro-derivative contains the nitro-group in the para-position; since, when treated with alcoholic potash, it yields acetylparanitrophenylhydrazine, and this, when boiled with dilute hydrochloric acid, is converted into paranitrophenylhydrazine.

Dinitrophenylmethyloxybiazolone, $C_6H_3(NO_2)_2{\cdot}C_3H_3N_2O_2$, is obtained by gradually adding fuming nitric acid to phenylmethyloxybiazolone dissolved in concentrated sulphuric acid. It melts at 127°, and closely resembles the mononitro-compound.

Paramidophenylmethyloxybiazolone, $NH_2{\cdot}C_6H_4{\cdot}C_3H_3N_2O_2$, is obtained, together with paraphenylenediamine hydrochloride, by warming nitrobiazolone with tin and hydrochloric acid. It crystallises in colourless needles, and melts at 125°. The *hydrochloride* crystallises in leaflets, and melts at 220°. The *platinochloride* crystallises in golden prisms, and does melt at the boiling point of sulphuric acid. The *sulphate* decomposes at 250°. The *nitrate* melts at 180°. The *acetyl* compound crystallises in colourless needles, and melts at 194°. The *benzoyl* compound crystallises in colourless tablets, and melts at 207—208°.

Diparaphenylmethyloxybiazolonethiocarbamide,

$$CS(NH{\cdot}C_6H_4{\cdot}C_3H_3N_2O_2)_2,$$

is obtained by the action of carbon bisulphide on an alcoholic solution of the base containing potassium hydroxide. It crystallises in yellow leaflets, and melts at 208°.

Monoparaphenylmethyloxybiazolonethiocarbamide, obtained by boiling the hydrochloride of the base with ammonium thiocyanate, crystallises in needles, and melts at 203°. *Paraphenylmethyloxybiazolonecarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}C_3H_3N_2O_2$, melts at 193°. *Diparaphenylmethyloxybiazolonecarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}C_3H_3N_2O_2)_2$, melts at 290°. *Phenylparaphenylmethyloxybiazolonethiocarbamide* melts at 170°.

Paramidoacetylphenylhydrazine, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}NHAc$, is obtained by boiling amidophenylmethyloxybiazolone with an aqueous solution of barium hydroxide in the absence of air. It crystallises in colourless leaflets, and melts at 146°. The *acetyl* compound,

$$NHAc{\cdot}C_6H_4{\cdot}NH{\cdot}NHAc,$$

crystallises in brownish needles, and melts at 221°.

Parahydrazidophenylmethyloxybiazolone hydrochloride,

$$C_3H_3N_2O_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2,HCl,$$

is obtained by diazotising the amidobiazolone, pouring the product into a concentrated solution of sodium sulphite, and warming the mixture with zinc-dust and acetic acid until it is colourless. It crystallises in colourless leaflets, and melts at 220°. E. C. R.

Xanthine Derivatives. By P. Balke (*J. pr. Chem.* [2], **47**, 537—567).—The behaviour of the xanthine derivatives with Fehling's solution in the presence of hydroxylamine hydrochloride, as a reducing agent, has been examined. The precipitates obtained in this way with guanine and xanthine are at first white, but speedily become green by oxidation, so that when analysed they show a composition intermediate between a cuprous oxide and a cupric oxide compound. There is sufficient evidence, however, to justify the view that the white precipitate is a compound of equal molecular proportions of the base and cuprous oxide. Heteroxanthine and paraxanthine, prepared from urine by Salomon's process, detailed in the paper, give similar white precipitates. Theobromine and caffeïne are the only known xanthine derivatives which do not give precipitates by the above reaction. The uric acid precipitate, $C_5H_4N_4O_3,Cu_2O$, is yellowish-white at first, but speedily becomes greenish; the carmine precipitate, $C_5H_4N_4O_3,Cu_2O$, is liable to be mixed with uncombined cuprous oxide which colours it yellow. The adenine and hypoxanthine precipitates are white.

The author proposes to take advantage of the great insolubility of these cuprous oxide compounds for the titration of xanthine derivatives, as has, indeed, been already done for the titration of uric acid. To an alkaline solution of the xanthine derivative, a few cubic centimetres of a solution of hydroxylamine hydrochloride are added, and then Fehling's solution is run in gradually from a burette, the liquid being constantly agitated until the yellow or yellowish-red colour of cuprous oxide makes its appearance, indicating that all the xanthine derivatives have been precipitated. A short interval should be allowed to elapse between each addition of the Fehling's solution, as the separation of the precipitate (or of cuprous oxide) is not very rapid. The results are calculated on the basis that 1 mol. of the derivative is equivalent to 2 atoms of copper; they are not trustworthy for solutions containing less than 1 per cent.

As a means of separating the xanthine derivatives from flesh, the production of the cuprous oxide precipitate compares very favourably with Neubauer's method; a description of how it may be applied is given. A process is also described for extracting the xanthine derivatives from plants, particularly malt sprouts, by means of this reaction.

The reason why very small quantities of sugar in urine are liable to escape detection by the reduction test is the fact that as soon as the cuprous oxide is produced in the hot liquid it combines with xanthine derivatives present, and is no longer recognisable as cuprous oxide.

Protamine, the base isolated by Miescher (this Journal, 1874, 794: 1875, 566), gives the biuret reaction with sodium hydroxide and copper sulphate, but, in the presence of hydroxylamine hydrochloride, a yellow precipitate is obtained which has all the characteristics of a cuprous oxide compound, and yields the original base when treated with hydrogen sulphide. It must be admitted, therefore, that protamine is an individual compound.

The *monosodium derivative* of xanthine, $C_5H_3N_4O_2Na + H_2O$, crystallises in microscopic needles from a solution of the base in the smallest possible quantity of sodium hydroxide. Like monosodium urate, it is decomposed by repeated recrystallisation, and retains its water of crystallisation at a high temperature (190—200°). The author discusses the position of the sodium in the molecule, and is still engaged in the investigation of the action of methylic iodide on the compound.

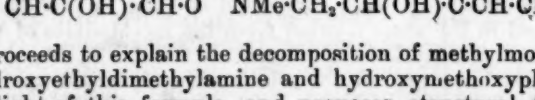
Episarkine, $C_4H_6N_2O$, is a new base obtained, together with hypoxanthine, when extracting the latter from urine by Salomon's method; it crystallises in prismatic needles, and is less soluble than hypoxanthine, from which it is best separated by dissolving the mixture in as dilute ammonia as possible and saturating the solution with carbonic anhydride, whereon the new base crystallises out. The yield was 0·4 gram from 1600 litres of urine. When evaporated with nitric acid and chlorine, the base remains white, and is not changed by ammonia; when evaporated with concentrated hydrochloric acid and potassium chlorate, a white residue is obtained which becomes intensely violet in an atmosphere of ammonia. One part of episarkine dissolves in 13,000 parts of cold water (no temperature given). The *hydrochloride* crystallises readily, in needles, from a hydrochloric acid solution of the base. No insoluble sodium derivative was obtained. With silver nitrate, the base gives a white precipitate insoluble in nitric acid, but soluble in ammonia. White precipitates were obtained with phosphotungstic acid, mercuric chloride, and ammoniacal lead acetate. The base resembles adenine, except in its great insolubility in cold water.

The paper concludes with a table exhibiting the reactions of the xanthine derivatives. A. G. B.

Constitution of Morphine. By G. N. Vis (*J. pr. Chem.* [2], **47**, 581—591; compare Knorr, Abstr., 1889, 905).—The author summarises the known facts with regard to morphine, and the conclusions to be drawn from them, as follows:—(1.) The nitrogen atom in morphine has a methyl group attached to it (Abstr., 1889, 417). (2.) Morphine is a tertiary base. (3.) Morphine yields pyridine in several reactions, and, therefore, probably contains a pyridine ring (compare Knorr, *loc. cit.*). (4.) Morphine derivatives easily pass into phenanthrene derivatives (Abstr., 1882, 1112; *loc. cit.*), indicating either the presence of a phenanthrene nucleus or an unusual predisposition for the production of one. (5.) By suitable oxidation, morphine yields picric acid, and by fusion with caustic alkali, protocatechuic acid; both reactions indicate a benzene ring, and the latter suggests analogy of constitution with that of papaverine, which so readily yields proto-

catechuic acid. (6.) Morphine contains two hydroxyl groups (Abstr., 1884, 615), one of which has phenolic functions, the other alcoholic functions. The third oxygen atom in morphine is indifferent, and apparently of an ethereal nature. (7.) The hydroxyl group which is apparently alcoholic retains its character in methylmorphimethine (Abstr., 1889, 417), and also, it would seem, in the hydroxyethyldimethylamine.

Ill-content with Knorr's formula for morphine (Abstr., 1889, 905), the author suggests the following as being in accord with the above facts:—

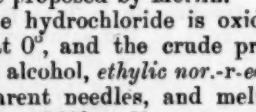


He proceeds to explain the decomposition of methylmorphimethine into hydroxyethyldimethylamine and hydroxymethoxyphenanthrene in the light of this formula, and proposes structural formulæ for pseudo- and apo-morphine. A. G. B.

Formula of Tropine. By J. F. Eykman (*Ber.*, **26**, 1400—1403).—By comparison of the molecular refraction of tropine and pseudotropine with that of certain substances of, in some respects, similar constitution, the conclusion is drawn that these two compounds do not, as Ladenburg thinks (this vol., i, 426), contain a double bond. C. F. B.

nor.-r-Ecgonine. By A. Einhorn and A. Friedlaender (*Ber.*, 26, 1482—1491).—In this paper, the constitutional formulæ adopted are based on those proposed by Merlin.

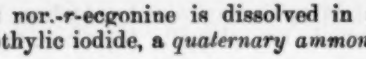
When *r*-ecgonine hydrochloride is oxidised with alkaline permanganate solution at 0°, and the crude product boiled with sulphuric acid and absolute alcohol, *ethylic nor.*-r-*ergonine*, which crystallises in colourless, transparent needles, and melts at 137°, is obtained; the *methylic* salt melts at 160°. *Nor.*-r-*ecgonine*,



is obtained by boiling either of the last-mentioned salts with water in a reflux apparatus for 12 hours; when pure, it crystallises in colourless needles. It is very insoluble in most solvents, its aqueous solution is without action on litmus, and metallic salts could not be obtained, but it forms crystalline salts with acids. *Ethylic nitroso-nor.*-r-*ecgonine* is an oily compound. The authors also find that the benzoyl derivative of ethylic cocaylhydroxyacetate (Abstr., 1889, 169) yields an oily *nitroso*-compound, and they therefore regard cocaylhydroxyacetic acid as nor.-*l*-ecgonine.

Ethylic benzoyl-nor.-r-*ecgonine* melts at 127°, and the *platinochloride* melts at 142°. *Benzoyl-nor.*-r-*ecgonine* is obtained by boiling the ethylic salt with water. Unlike the corresponding derivative of the *l*-series, neither a copper nor a silver salt could be obtained from it.

When ethylic nor.-*r*-ecgonine is dissolved in ethylic acetate and treated with methylic iodide, a *quaternary ammonium iodide*,



melting at 178° is obtained; when an aqueous solution of this is shaken with silver chloride, the *methochloride* is formed as an oil; it yields an *aurochloride* melting at 182°. The methiodide just described seems also to be obtained by the action of methylic iodide on ethylic *r*-ecgonine. When the methiodide from either source is boiled with dilute sodium hydroxide, dimethylamine and an *acid*, $C_9H_8O_2$, melting at 55—56° is obtained. This compound is being further studied; it is also formed in the same manner from the methiodides of methylic *r*-ecgonine, and of ethylic *l*-ecgonine.

The authors have proved the relationship of nor.-*l*-ecgonine to *r*-ecgonine to be that above shown, by the fact that the former is converted into the latter on methylation. A. R. L.

Ptomaïnes. By A. Garcia (*Zeit. physiol. Chem.*, **17**, 543—595).—In putrefying mixtures of horseflesh and pancreas, hexamethylenediamine, $C_6H_{16}N_2$, occurs in addition to the diamines already described.

Ptomaïnes may be best estimated by Baumann's benzoic chloride method. In mixtures, the presence of sugar reduces the formation of diamines to about half; the same diamines are, however, formed.

The production of putrescine, cadaverine, and hexamethylenediamine is an early phenomenon in such putrefying mixtures at a favourable temperature; it reaches its highest point within about three days, and they are produced in the same proportion throughout. In cystinuria, tetramethylenediamine only is produced in the later stages. Feeding on cheese causes an increase, on carbohydrate a diminution, in diamine production. Infection of nutritive media with the fæces of such patients causes the appearance of ptomaïnes. In media not so infected, exclusion of air hinders the formation of diamines during the first few days (four days in the experiments which are described). W. D. H.

Urobilin. By A. Eickholz (*J. physiol.*, **14**, 326—339).—Normal urobilin exists in the urine totally or partially as chromogen, and can by appropriate methods be isolated so as to furnish a solution containing the pigment wholly or partly as chromogen. Urobilin and urochromogen are not highly coloured, and the urine cannot depend on them to any great extent for its colour. Pathological urine contains an additional pigment, *pathological urobilin* with a different absorption spectrum; it also can be isolated as a chromogen. Both urobilins can be reduced by sodium amalgam, but the reduction product differs from urochromogen, and may be termed *urobilinogen*. On prolonged reduction, bilirubin furnishes a substance resembling urobilin. Maly's hydrobilirubin is an intermediate product in the reduction. Hæmatin in acid solution is reduced to a substance closely

resembling urobilin. Incomplete reduction furnishes a substance also resembling urobilin, but which immediately reverts to the state of urohæmatoporphyrin on standing. W. D. H.

Urinary Colouring Matters. By H. Rosin (*Chem. Centr.*, 1893, i, 487—488; from *Deut. Med. Woch.*, **19**, 51—54).—The red colouring matter obtained in Rosenbach's reaction can not only be isolated in the crystalline form from urine, but also from the vegetable organism (and from indigo-blue). It is named by the author indigo-red.

When urine is heated with nitric acid, a reddish coloration is produced; this has been observed, in the case of pathological urine, by Nencki and Sieber. The colouring matter is obtained by heating urine, previously decolorised with basic lead acetate or animal charcoal, with an acid and an oxidising agent. Nitric acid alone (not chromic acid) can be used, or hydrochloric or sulphuric acid in the presence of hypochlorite, avoiding an excess of the latter. It is soluble in amyl alcohol, but insoluble in ether, chloroform, and benzene. It has acidic properties, and exhibits a characteristic absorption spectrum which is identical with that observed by Nencki and Sieber for uroroseïn. The colouring matter occurs in larger quantity in pathological than in normal urine.

In order to obtain the substance from which the colouring matter is produced, ox-urine is precipitated with basic lead acetate and the filtrate treated with ammonia; the precipitate is collected, dried at 70°, extracted with absolute alcohol, the lead removed from the alcoholic solution by hydrogen sulphide, and the filtrate concentrated and fractionally precipitated with ether. The chromogen crystallises from the ethereal alcoholic solution in colourless, transparent needles soluble in water. A. R. L.

Vegetable Nucleïn. By P. Petit (*Compt. rend.*, **116**, 995—997).—Malt combs (Touraillons) containing a large proportion of germs mixed with radicles are heated at 60° for some minutes with a 1 per cent. solution of potassium hydroxide. The liquid is filtered, allowed to cool, and exactly neutralised with dilute hydrochloric acid, when a greyish precipitate forms and rapidly agglomerates. It is washed with water, then with alcohol and ether, and is dried over sulphuric acid. It forms brown-black fragments with a conchoïdal fracture, and has the composition C, 43·18; H, 6·64; N, 12·86; P, 1·11; Fe, 0·195; ash, 6·2; SiO_2, 3·2; O, 31·1 = 100. Unlike the animal nucleïns, described by Kossel, Liebermann, and others, it contains no sulphur.

When placed in solutions of sodium chloride, vegetable nucleïn swells up and becomes greyish; it gives no reaction with Millon's reagent, but is dissolved by alkalis. When mixed with ammoniacal potassium ferrocyanide and then with excess of acetic acid, it yields a white precipitate which gradually becomes blue, the change being more rapid the more concentrated the acid and the higher the temperature. With hydrochloric acid, the change to blue is almost instantaneous. Tannin gives a white precipitate which blackens on heating. The two last reactions are regarded by Bunge as general for all nucleïns.

When the nucleïn from barley is heated with water under a pressure of 4 atmos., it dissolves and yields a pale-yellow solution on which *Aspergillus* or *Penicillium* grows with extreme rapidity.

The solution gives with ferrocyanides and with tannin the same reactions as the original compound, but it is not precipitated by acids. With ammoniacal silver nitrate it yields a grey precipitate which blackens when heated, and with copper sulphate it yields, when heated, an amorphous, grey precipitate. When boiled for a long time with nitric acid, it dissolves completely, and yields oxalic acid and an acid that forms a crystalline compound with phenylhydrazine.

Vegetable nucleïn is absorbed by many plants, and particularly by barley. A solution of it seems to be a particularly advantageous means of supplying to barley the iron that is indispensable for its proper development. C. H. B.

The Filtration of Caseïn Solutions through Porcelain. By L. Hugounenq (*Ann. Chim. Phys.* [6], **28**, 528—537).—Porcelain filters allow albuminous substances to pass through them very unequally; asbestos porcelain is traversed more easily than the biscuit of the Chamberland tubular filters. Some proteïds leave a residue on the exterior surface of the filter which never passes through; a small quantity remains fixed in the pores of the septum and resists washing with water. In the estimation of proteïds, 12—15 per cent. loss may occur in this way. The filtration of certain albuminous substances through porcelain is accompanied by chemical changes. Gas is evolved, and caseïn, precipitable by acetic acid, passes through to the extent of one-third its total amount. The asbestos or ordinary porcelain filters only allow the precipitable caseïn to pass through when the alkalinity of the solution corresponds with a value requiring 1·5 grams of sulphuric acid per litre to neutralise it, and even then a considerable residue remains behind; this can only be avoided by rendering the solution more strongly alkaline. The chemical composition of a culture medium containing proteïds gives no indication as to its chemical composition after sterilisation by means of the tubular filter. A. R. L.

Organic Chemistry.

Action of Mineral Acids on Dimethylallene. By I. Kondakoff (*J. Russ. Chem. Soc.*, **24**, 513—515).—The author showed (*J. Russ. Chem. Soc.*, **21**, 36) that fuming hydrochloric acid acted on dimethylallene with formation of the unsaturated chloro-derivative, $CMe_2Cl{\cdot}CH{:}CH_2$, and of a saturated dichloro-derivative to which he attributed the constitution $CMe_2Cl{\cdot}CH_2{\cdot}CH_2Cl$. He now proves the correctness of the last formula by preparing the corresponding glycol by heating the dichloride for 20 hours with aqueous potash. The glycol, $C_5H_{10}(OH)_2$, is a syrup having the sp. gr. 0·9951 at 0° and 0·9892 at 20°. It has a caustic, cooling taste, and boils at 202—203°. On oxidation with 1 per cent. potassium permanganate solution, it yields β-hydroxyvaleric acid, with traces of glyoxylic, acetic, and formic acids.

J. W.

Cyanogen. By T. Zettel (*Monatsh.*, **14**, 223—232).—The products of decomposition of this substance have again been studied, and, in the main, the results of previous observers have been confirmed. When solutions of cyanogen in acetic acid or dilute acetic, hydrochloric, or sulphuric acids are allowed to remain at the ordinary temperature, no change takes place. A solution in concentrated hydrochloric acid, when kept at the ordinary temperature, yields, chiefly, oxamide, together with some ammonia and oxalic acid, whilst a solution in dilute hydrochloric acid (one-fifth), heated for six hours at 150°, gives oxalic acid, ammonia, and some carbonic anhydride. A solution in 10 per cent. aqueous potash decomposes at the ordinary temperature, yielding azulmic, hydrocyanic, and isocyanic acids, together with ammonia and carbonic acid, but no oxalic acid. An aqueous solution yields at the ordinary temperature, or more quickly at 100°, azulmic acid, oxalic acid, ammonia, carbonic anhydride, hydrocyanic acid, and carbamide.

C. F. B.

Hydrolysis of Aromatic Nitriles. By L. Bouveault (*Bull. Soc. Chim.* [3], **9**, 368—373).—The process consists in converting the nitrile into the corresponding amide by digesting it with 85 per cent. sulphuric acid (or 90 per cent. if it be insoluble in acid of 85 per cent. strength) at 100°, dissolving the amide in cold, strong sulphuric acid and adding a concentrated aqueous solution of the calculated quantity of sodium nitrite, in such manner that the temperature shall not rise above 30—40°; a few moments at a temperature of 40—50° will complete the quantitative conversion of the amide into the acid.

A. G. B.

Sodium Platinocyanide. By T. Wilm (*Zeit. anorg. Chem.*, **4**, 298—299; compare Abstr., 1886, 604).—This salt may readily be prepared from the mother liquor of a preparation of the potassium salt by precipitating as copper platinocyanide and heating this with a slight excess of soda solution. It crystallises with $3H_2O$ in long,

lustrous, colourless, transparent prisms or needles. These are stable in the air, and become anhydrous at 120—125°. The crystals do not fluoresce like those of the potassium salt, nor are they altered by chlorine under the same conditions as those under which the chlorine compound of the potassium salt is formed (Abstr., 1889, 951).

A. G. B.

Fulminic acid and its Derivatives. By R. Scholl (*Chem. Centr.*, 1893, i, 730—731).—The author gives a historical survey of fulminic acid, and discusses the various formulæ which have been suggested for it; he considers, with Steiner, that its properties and modes of formation are best explained on the assumption that it is dioximidoethylene, NOH:C:C:NOH.

Bromonitromethane, $CH_2Br{\cdot}NO_2$, is formed by the action of cyanogen bromide on sodium nitromethane. *Iodoacetonitrile*, $CN{\cdot}CH_2I$, can be prepared by heating chloracetonitrile with potassium iodide and methyl alcohol, and is a colourless, heavy oil, volatile with steam, boiling at 76—77° under a pressure of 12 mm., and at 182—184° with decomposition under 720 mm. pressure; its vapour attacks the eyes, and it produces burns when brought into contact with the skin. By the action of silver nitrite on the preceding compound, two substances are formed; one, $C_3H_2N_2O$, which is crystalline, melts at 72—73°, and is being further investigated; the second is a colourless, viscid liquid boiling at 160—162° under a pressure of 12 mm. The compound does not appear to have acidic properties, and as on treatment with sodium ethoxide or with benzylamine, a nitro-group is eliminated, it may be represented by the formula $CN{\cdot}C(NO_2){:}NO{\cdot}CH_2{\cdot}CN$. Diiodonitroacetonitrile and dibromonitroacetonitrile are represented by the formulæ $C_2N_2O_2I_2$ and $C_2N_2O_2Br_2$ respectively; the latter does not combine with hydrogen sulphide, and on treatment with hydrochloric acid is resolved into hydrogen bromide, hydroxylamine, oxalic acid, and a little ammonia; it is therefore not a direct substitution product of mercuric fulminate, and probably has the formula

$$\begin{matrix} CBr{:}N{\cdot}O \\ | \\ CBr{:}N{\cdot}O \end{matrix}$$

J. B. T.

Normal Amyl Alcohol. By L. Tissier (*Bull. Soc. Chim.* [3], **9**, 100—101).—Wischnegradski's inference that this alcohol is contained in fermentation amyl alcohol, because the amylene derived from the latter contains symmetrical methylethylethylene, is erroneous, for the author was unable to isolate any of the normal alcohol from 1600 litres of fusel oil. The methylethylethylene was doubtless formed from active amyl alcohol by molecular transformation, and, as an experiment showed, it can actually be obtained in considerable quantity by allowing this alcohol to flow over fused zinc chloride contained in an iron tube.

C. F. B.

Fourth Primary Amylic Alcohol. By L. Tissier (*Ann. Chim. Phys.* [6], **29**, 321—389).—An account of the preparation and properties of the primary amylic alcohol trimethylcarbincarbinol has already been published (Abstr., 1891, 998). In the present

memoir, the author gives his work in detail and describes several new derivatives of trimethylethylic alcohol.

The *glycol*, $CMe_3 \cdot CH(OH) \cdot CH(OH) \cdot CMe_3$, is formed by the action of sodium amalgam on trimethylacetaldehyde; it was also separated from the portion of the reduction product of trimethylacetic chloride (*loc. cit.*) boiling above 180°. It crystallises in tables, melts at 83—84°, boils at 185—187°, has the odour of pinacone, and is slightly soluble in water; when treated with one equivalent of acetic acid (m. p. 16·6°), 27·56 per cent. of the latter is converted into the acetate.

Trimethylethylic chloride is obtained by chlorinating tetramethylmethane; also by saturating trimethylcarbincarbinol cooled below 0° with hydrogen chloride, or by the action of phosphoric chloride on the same alcohol; it is a colourless, mobile liquid of agreeable odour, partially decomposes when distilled, and has a sp. gr. of 0·8792 at 0°: an *amylbenzene* boiling at 185—190° is formed when the chloride is treated with benzene and aluminium chloride (compare Schramm, Abstr., 1889, 127). The *bromide*, $CMe_3 \cdot CH_2Br$, is a liquid of sp. gr. 1·2253 at 0°, boils at 108—109°, and when heated with alcoholic potash yields *trimethylethylene*, $CMe_2{:}CHMe$, the *dibromide* of which boils at about 175°. The *iodide*, $CMe_3 \cdot CH_2I$, has a sp. gr. of 1·0502 at 0°, and boils at 127—129° with decomposition; the distillate yields an *acetate* boiling at 124°, which on hydrolysis is converted into tertiary amylic alcohol.

Trimethylethylic acetate, $CMe_3 \cdot CH_2 \cdot OAc$, is a colourless liquid of sp. gr. 0·86453 at 0°, and boils at 126°; the *propionate* has a sp. gr. of 0·87327 at 0°, and boils at 147—148°; the *butyrate* has a sp. gr. of 0·87193 at 0°, and boils at 165—166°; the *isobutyrate* has a sp. gr. of 0·86957 at 0°, and boils at 158—159°; the *trimethylacetate* has a sp. gr. of 0·86078 at 0°, and boils at 162—164°; and the *benzoate* boils at 139—141°.

When excess of sulphuric acid is added by degrees to trimethylcarbincarbinol, the *amylsulphuric acid* is formed.

Trimethylethylamine, $CMe_3 \cdot CH_2 \cdot NH_2$, is obtained by reducing an alcoholic solution of trimethylacetonitrile with sodium; it boils at 81—82°; the *hydrochloride* is a colourless substance which melts with decomposition at about 85°; the *platinochloride*, *aurochloride*, and *mercurochloride* were also prepared.

The trimethylacetic acid employed in this research was prepared by the oxidation of pinacolin with potassium dichromate and dilute sulphuric acid. It has, therefore, been necessary to prepare large quantities of pinacone; the method used was the action of sodium on acetone floating on a solution of potassium carbonate, and the author has examined the oily bye-product insoluble in water obtained in the latter reaction. Two compounds were isolated from this bye-product: mesityl oxide (b. p. 130—132°), and a *compound* $C_9H_{14}O$, boiling at 129—133° under a pressure of 4 mm., and at 220—230° with decomposition under the ordinary pressure; the *oxime*, $C_9H_{14} \cdot NOH$, is a colourless, crystalline compound melting at 102° and boiling at 155—160° (4 mm.).

New methods of preparing trimethylacetic chloride, trimethyl acetamide, and trimethylacetonitrile are described. A. R. L.

Allylmethylethylcarbinol. By N. Saytzeff (*J. Russ. Chem. Soc.*, **24**, 468—471).—A mixture of methyl ethyl ketone (300 grams) and allylic iodide (750 grams) was added drop by drop to freshly heated granulated zinc contained in a retort surrounded by ice-cold water; on the following day, the product was decomposed with water and distilled. The oily layer was then separated from the aqueous layer, dried with fused potash, and submitted to fractional distillation, 70 grams of an alcohol boiling between 135° and 145° being obtained. This yielded 20 grams of pure *allylethylmethylcarbinol* boiling at 138·5—139·5° under a pressure of 753 mm. It is a colourless oil having a specific gravity of 0·8586 at 0°/0° and 0·84315 at 20°/20°. Its *acetate* boils at 158—160° and has the sp. gr. 0·8943 at 0°/0°.

The corresponding *glycerol*, $C_7H_{13}(OH)_3$, was obtained by oxidising the carbinol with potassium permanganate, filtering, evaporating on the water-bath, and extracting with alcohol. It is a colourless, viscous liquid, easily soluble in water, alcohol, and ether. The *triacetate* was prepared by heating the glycerol with acetic anhydride for three hours at 120°, and forms a liquid which is soluble with difficulty in water, but dissolves readily in alcohol and ether. J. W.

Allylmethylhexylcarbinol. By A. Boyanus (*J. Russ. Chem. Soc.*, **24**, 471—473).—Allylmethylhexylcarbinol was prepared from methyl hexyl ketone (98 grams) and allylic iodide (130 grams) by the action of zinc (compare preceding abstract). The portion of the resulting oil that boiled at 215—216° was the required product. On oxidation with permanganate, it yielded the *glycerol*, $C_{11}H_{21}(OH)_3$, which, on treatment with acetic anhydride, was converted into the triacetate, $C_{11}H_{21}(OAc)_3$. J. W.

Action of Acetic Anhydride on Linalol. By G. Bouchardat (*Compt. rend.*, **116**, 1253—1255).—Linalol obtained from *Lavandula spica* seems to be identical with licareol (this vol., i, 493 and 495). When treated with acetic anhydride at the ordinary temperature, it yields an acetate which regenerates linalol on saponification, but if heated at 100—120° a different acetate is formed, which, when saponified, yields a new alcohol, analogous to or identical with licarhodol. This acetate boils at 120—125°, under a pressure of 25 mm., and is optically inactive; sp. gr. at 0° = 0·9377—0·9467. When saponified with alcoholic potash at 100°, it yields a neutral compound $C_{10}H_{18}O$, which, under normal pressure, boils at 226—231° with slight decomposition; sp. gr. at 0° = 0·9061; it has an odour of roses, is optically inactive, combines readily with bromine, and yields an inactive dihydrochloride of sp. gr. 1·046. This alcohol, and therefore licarhodol also, seems to be identical with the geraniol obtained from Indian essential oil of geranium. C. H. B.

Licarhodol from Licareol. By C. Barbier (*Compt. rend.*, **116**, 1200—1202).—The acetate which is obtained, together with licarene, by the action of acetic anhydride on licareol, can readily be purified by fractionation under low pressure. It has the empirical formula $C_9H_{15}\cdot CH_2\cdot OAc$, and is a colourless liquid with a strong odour of

angelica. It boils at 135° under a pressure of 21·5 mm.; sp. gr. at 0° = 0·9298; refractive index at 19·5° for λ 645 = 1·4594, and for λ 452·6 = 1·4734. It acts feebly on polarised light, a column 200 mm. in length giving a rotation of −0° 32′. The acetate is insoluble in water; it is rapidly saponified by alcoholic potash, and yields a new alcohol, *licarhodol*.

Licarhohol has the same composition, $C_{10}H_{18}O$, as licareol, but differs from it markedly in physical properties. It is a colourless, oily liquid, with a strong odour of roses, and is insoluble in water. It boils at 122° under a pressure of 19 mm.; sp. gr. at 0° = 0·8952; refractive index at 15·3° for λ 645 = 1·4740, and for λ 452·6 = 1·4893; rotatory power of a column 200 mm. long = −1° 14′ at 20·4°.

When oxidised, licarhodol yields an aldehyde identical with that obtained from licareol, and when it is treated with energetic oxidising agents, the products are the same as from licareol. With dry hydrogen chloride, it yields a dihydrochloride, $C_{10}H_{18}Cl_2$, identical with the dihydrochloride of licarene.

It follows that licarhodol is a stable stereoisomeride of licareol, the two being distinguished by their behaviour with acetic anhydride. This result confirms the constitution previously attributed to licareol. (See this vol., i, 495, 496.) C. H. B.

Ethylmethylpropylethylene Glycol. By I. Panfiloff (*J. Russ. Chem. Soc.*, **24**, 473—477).—Methyldipropylcarbinol, boiling at 159—161°, was saturated in the cold with hydrogen chloride, allowed to remain for 24 hours, and then poured into cold water. From 58·5 grams of alcohol there were obtained in this way 66 grams of the corresponding chloride, which was then dropped into a solution of 75 grams of potash in 150 grams of alcohol heated on the water-bath. The heating was continued for four hours, the mixture then being distilled almost to dryness. On treating the distillate with water, about 45 grams of an oily product were obtained, which, on fractionation, gave 28·5 grams of a hydrocarbon, C_8H_{16}, boiling between 118° and 121°. This hydrocarbon (20 grams) was oxidised in the cold with 1 per cent. potassium permanganate solution, the product distilled with steam, whereby half the original octylene was recovered, filtered, neutralised with sulphuric acid, and distilled to a small bulk. From the second distillate 10 grams of a viscid liquid was extracted with ether, and this on fractionation gave 4 grams of a substance, $C_8H_{16}(OH)_2$, boiling between 210° and 215°. Propionic and acetic acids were also found in the oxidation product. As Sokoloff has shown the hydrocarbon C_8H_{16} to be CMePr:CHEt, the glycol must have the constitution CMePr(OH)·CHEt(OH).

J. W.

Birotation of Glucose. By B. Tollens (*Ber.*, **26**, 1799—1802).—In a recent paper (*Bull. Soc. Chim.* [3], **9**, 401, 511), Béchamp ascribes the property of birotation shown by solutions of glucose to the fact that in the freshly prepared solutions the sugar is present as hydrate, and that the hydrate gradually dissociates, until, after 24 hours, it is all present in the form of anhydrous glucose. The author has long been engaged on experiments with the view of ascertaining the

cause of the birotation, and has come to a conclusion identical with that of Béchamp. He has found that anhydrous glucose dissolves in water and in dilute ammonia with absorption of heat in the first instance, but in the case of the aqueous solution a rise of temperature quickly follows, and the solution shows the double rotatory power, which then gradually diminishes. No subsequent evolution of heat occurs with the ammonia solution, and the latter has the rotatory power shown by the aqueous solution after 24 hours. It follows, therefore, that the sugar which gives the double rotation is the hydrate, and that this gradually loses water on remaining, re-forming the anhydride. H. G. C.

Decomposition of Galactose by Calcium Hydroxide. By H. Kiliani and H. Sanda (*Ber.*, **26**, 1649—1655).—The product obtained by the decomposition of glucoses by caustic alkalis or alkaline earths consists of about 14 per cent. of a saccharine, 41 per cent. of lactic acid, and a residue of about 50 per cent., the nature of which is unknown. In attempting to determine the composition of this residue, the authors have discovered an easy method of preparing metasaccharin and a new saccharin, which they name *parasaccharin*.

Galactose (1 part) is dissolved in water (10 parts), calcium hydrate (0·5 part) added, and the mixture allowed to remain four weeks in a tightly closed flask, when it is filtered, and the filtrate heated to boiling for three hours. It is then saturated with carbonic anhydride, again filtered, concentrated, and allowed to crystallise in a cool place. In about 10 days, 14 per cent. of calcium saccharinate separates out. The authors were unable to obtain metasaccharin by boiling a solution of galactose with lime. On concentrating the solution of calcium salts, they were unable to obtain the smallest trace of calcium isosaccharinate (Cuisinier, *Mon. Sci.*, 1882, 521).

The mother liquors of the calcium metasaccharinate were precipitated with oxalic acid, and extracted with ether. In this way an acid syrup, insoluble in ether, was obtained, which when partially neutralised with barium carbonate and mixed with alcohol, yielded a crystalline barium salt, containing a new saccharinic acid mixed with some barium metasaccharinate. The latter is separated as follows: the barium salts are decomposed with sulphuric acid, the solution evaporated to a syrup and mixed with alcohol, when metasaccharin separates. By converting the uncrystallisable residue into calcium salt and adding alcohol, the last traces of calcium metasaccharinate crystallise out.

Parasaccharin has almost the same rotatory power as metasaccharin. Under the same conditions metasaccharin gave $[\alpha]_D = -27{\cdot}7°$, parasaccharin $[\alpha]_D = -26{\cdot}1°$. The barium salts cannot be distinguished from each other. Calcium parasaccharinate, however, does not crystallise, whereas the calcium metasaccharinate crystallises very readily. Moreover, parasaccharinic acid does not yield a crystalline phenylhydrazide.

When the syrup obtained by decomposing pure barium parasaccharinate with sulphuric acid is boiled with hydriodic acid, α-ethylbutyrolactone is obtained. When parasaccharinic acid is heated

with silver oxide, it yields carbonic anhydride, glycollic acid, and a small quantity of an intermediate compound. E. C. R.

Absence of Spontaneous Inversion of Cane Sugar in Aqueous Solution at the Ordinary Temperature, and the Cause of its Apparently Spontaneous Inversion under the Action of Light. By A. Béchamp (*Bull. Soc. Chim.* [3], **9**, 21—27).—In every case where the author found that inversion of cane sugar had taken place, organisms were present. The organisms concerned in the inversion are not entirely destroyed by boiling the solutions nor even by the addition of phenol. Ordinary white loaf sugar gives solutions which show greater inversion than solutions of the purest sugar-candy similarly treated, owing to the small quantities of proteïd and mineral matters contained in the former favouring the growth of the organisms. The exposure to sunlight of sealed tubes containing samples simply favours the growth of the organisms by raising the temperature of the containing solution. W. T.

Recent Investigations on Carbohydrates. By W. E. Stone (*Chem. News*, **67**, 304—306).—A valuable *résumé* of the work in this subject during the past year.

Metaldehyde. By C. Friedel (*Bull. Soc. Chim.* [3], **9**, 384—385).—Tröger (this vol., i, 64) has observed the transformation of a sample of metaldehyde into paraldehyde. The author finds that when dry metaldehyde is heated in a sealed tube at 60—65° for some hours, it becomes converted into a mixture of paraldehyde with a little aldehyde. Recent work having shown that metaldehyde has the same molecular weight as paraldehyde, the author thinks that this new observation furnishes evidence that these two compounds are steoreisomerides, which may be represented by a triangle with the carbon atoms of the CHO groups of the three aldehyde molecules at its three angles, united in each case by an oxygen atom. The meta- and para-compounds will thus be *cis*- and *trans*-derivatives, according as the methyl groups are on one or other of the sides of the plane of the triangle. A. G. B.

Action of Sulphuric acid on the Pinacone of Methyl Ethyl Ketone. By P. Herschmann (*Monatsh.*, **14**, 233—244).—When this pinacone, OH·CMeEt·CMeEt·OH, is treated with concentrated sulphuric acid, the temperature being kept low, the pinacoline, $CEtO{\cdot}CMe_2Et$, boiling at 148—153°, is practically the sole product of the reaction. But if the pinacone is boiled with dilute sulphuric acid, then, in addition to the above-mentioned pinacoline, there is obtained a hydrocarbon, C_8H_{14}, boiling at 117—121°, which unites with four atoms of bromine, and seems to polymerise on standing, and also a substance boiling at 132—139°, which is probably the isomeric pinacoline $CMeO{\cdot}CMeEt_2$. C. F. B.

Solubility of Barium and Calcium Butyrate. By A. Deszáthy (*Monatsh.*, **14**, 245—254).—The solubility of the salts $(C_4H_7O_2)_2Ba$

+ $2H_2O$ and $(C_4H_7O_2)_2Ca + H_2O$ in water at various temperatures was determined by shaking the salt with water in an air-bath for 1½—2 hours, filtering the solution at the same temperature (by means of an arrangement described in detail), and estimating as sulphate the metal in the weighed filtrate. The numbers below give the parts of anhydrous salt which dissolve in 100 parts of water at the temperature indicated.

	0°.	10°.	20°.	30°.	40°.	50.	60°.
Ba salt....	37·42	36·65	36·12	35·85	35·82	36·44	37·68
Ca salt....	20·31	19·05	17·97	17·07	16·35	15·81	15·44

	70°.	80°.	118°.	127°.
Ba salt.....	39·58	42·13	—	—
Ca salt.....	15·34	15·34	18·12	19·83

C. F. B.

Solubility of the Lead Salts of Stearic and Palmitic acids in Ether. By A. Lidoff (*J. Russ. Chem. Soc.*, **24**, 524—526).—50 c.c. of anhydrous ether dissolves at the ordinary temperature 0·0074 gram of lead stearate (m. p. 122°) and 0·0092 gram of lead palmitate (m. p. 112°). J. W.

Behenic Acid. By Z. Talantzeff (*J. Russ. Chem. Soc.*, **24**, 502—504).—The author prepared behenic acid from iodobehenic acid (obtained by the addition of hydrogen iodide to erucic acid) by reduction in alcoholic solution with zinc and hydrochloric acid. The acid was purified by repeated recrystallisation from alcohol. In a capillary tube, it melted at 84° and solidified at 77—79°; when the thermometer was immersed in a mass of the acid, the melting point was 83° and the freezing point 79°. 100 parts of alcohol (30° Tralles) dissolve 0·102 part of behenic acid, whilst 100 parts of ether at 16° dissolve 1·922 parts of acid. J. W.

The Wax of Gum-lac. By A. Gascard (*J. Pharm.* [5], **27**, 365—372).—Gum-lac may be separated into three fractions, respectively insoluble, soluble on boiling, and soluble in the cold in 95 per cent. alcohol. The first contains, besides remains of insects and some nitrogenous substance, a small quantity of a wax melting at 92°; this is myricyl melissate, $C_{29}H_{59}\cdot COOC_{30}H_{61}$, and the myricyl alcohol obtained from it by hydrolysis is identical with that from carnauba wax and from beeswax, and melts at 88°, and not at 85° as Brodie stated. The second fraction, soluble in hot alcohol, contains rather more than 50 per cent. of free myricyl alcohol, and yielded on hydrolysis myricyl and a little ceryl alcohol, and palmitic, melissic, oleïc, and a little cerotic acid, together with some resinous acids having an aromatic odour. C. F. B.

New Method of preparing Acrylic acid. By C. Moureu (*Bull. Soc. Chim.* [3], **9**, 386—392).—Acrylic acid is best prepared by heating β-chloropropionic acid (1 mol.) with aqueous potash (over 2 mols.) in a reflux apparatus, the bulk of the liquid being about

1500 c.c. The acrylic acid is liberated by dilute sulphuric acid and distilled over.

Acrylic chloride is prepared by treating sodium acrylate with phosphoryl chloride. It is a colourless, fuming, acrid liquid, and boils at 75—76° at normal pressure; its sp. gr. at 0° is 1·14; water decomposes it easily, and it undergoes spontaneous alteration, of an undetermined nature, in course of time. By treatment with bromine in chloroform, it yields $\alpha\beta$-dibromopropionic chloride, which is a heavy, colourless liquid and boils at 191—193° with slight decomposition; its sp. gr. is 2·181 at 0°; it slowly becomes yellow, a change which occurs more rapidly in sunlight.

A. G. B.

Oxidation of β-Chlorcrotonic acids. By I. Kondakoff (*J. Russ. Chem. Soc.*, **24**, 508—513).—β-Chlorcrotonic acid (6 grams), when oxidised with 18 grams of potassium permanganate in 1 per cent. solution, yielded acetic acid (3·4 grams) and oxalic acid (1 gram). β-Chlorisocrotonic acid (10 grams), under the same conditions, also gave acetic acid (5 grams) and oxalic acid. No trace of an aldehyde was observed in either case when an insufficient quantity of permanganate was employed. These results are equally well explained, whether we assume crotonic and isocrotonic acids to be geometrically isomeric or not.

J. W.

Action of Sodium Hydrogen Sulphite and of Sulphurous acid on Oleïc and Erucic acids. By M. C. Saytzeff and A. Saytzeff (*J. Russ. Chem. Soc.*, **24**, 477—486).—Oleïc acid was heated with an equal weight of a saturated solution of sodium hydrogen sulphite for 10 hours at 175—180°. On cooling, the upper fatty layer crystallised to an easily fusible mass, which was purified by recrystallisation from 90 per cent. alcohol, and finally from ether. The pure substance melted in a capillary tube at 51—52°, and solidified at 40—45° when the thermometer was immersed in the fused substance. Analysis gave numbers agreeing with the formula $C_{18}H_{34}O_2$, and a study of the salts and oxidation products showed that the substance was elaïdic acid. The same acid is formed from oleïc acid by heating with sulphurous acid for 24 hours at 200°. Erucic acid when treated in the same way yields brassidic acid.

The authors explain the mechanism of the isomeric transformation by assuming the addition of $H{\cdot}SO_2OH$, rotation into the most favoured position, and subsequent removal of $H{\cdot}SO_2OH$.

J. W.

Isoerucic acid. By P. Alexandroff and N. Saytzeff (*J. Russ. Chem. Soc.*, **24**, 486—491).—Iodobehenic acid, prepared by the direct addition of hydrogen iodide to erucic acid, was gradually added to a solution of an equal weight of caustic potash in 2 parts of 95 per cent. alcohol heated on the water-bath. On completion of the reaction, the alcohol was distilled off, and the soap remaining behind decomposed by means of boiling dilute sulphuric acid. The solid acid obtained in this way was purified by repeated recrystallisation from alcohol, and is called by the authors *isoerucic acid*,

$C_{22}H_{42}O_2$. It melts in a capillary tube at 54—56°, and solidifies in mass at 54°. From alcoholic solution it separates in small, tabular crystals, but solidifies from the fused state in brilliant stellate aggregates, very like brassidic acid. It combines with bromine, giving a dibromide, $C_{22}H_{42}Br_2O_2$, which fuses at 44—46°, the corresponding compound from brassidic acid melting at 54—55°. On reduction with fuming hydriodic acid, it yields behenic acid. When oxidised in dilute alkaline solution with potassium permanganate, it gives a dihydroxy-acid, $C_{22}H_{44}O_4$, melting at 86—88°. The authors consider that erucic acid has the constitution $CH_3{\cdot}[CH_2]_{17}{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, and isoerucic acid, $CH_3{\cdot}[CH_2]_{17}{\cdot}CH_2CH{:}CH{\cdot}COOH$. J. W.

Transformation of Elaïdic acid into Oleïc and Iso-oleïc acids. By I. Lebedeff (*J. Russ. Chem. Soc.*, **24**, 492—495).—The iodo-acid formed by the direct addition of hydrogen iodide to elaïdic acid, if treated with alcoholic potash, gives a mixture of oleïc and of iso-oleïc acids, which may be separated by treating the lead salts with ether.

The iso-oleïc acid obtained in this way melts at 43—45°. On oxidation with potassium permanganate, it gives an acid $C_{18}H_{36}O_4$, melting at 78—80°. The same acid is obtained by treating the dibromide with moist silver oxide. The author considers that these results confirm the view that oleïc and elaïdic acids are geometrical isomerides. J. W.

Transformation of Brassidic acid into Erucic and Isoerucic acids. By N. Saytzeff (*J. Russ. Chem. Soc.*, **24**, 496—499).—By the addition of hydrogen iodide, brassidic acid may be converted into an iodobehenic acid which, when treated with alcoholic potash, yields the potassium salts of erucic and isoerucic acids. The former is only present in small quantity, isoerucic acid being the chief product of the reaction. The iodobehenic acid prepared from erucic acid yields exactly the same products. J. W.

Oxidation of Brassidic acid. By M. Jukovsky (*J. Russ. Chem. Soc.*, **24**, 499—501).—When brassidic acid is treated with an equal quantity of potassium permanganate and 30 per cent. of caustic potash in 1·5 per cent. aqueous solution, the reaction proceeds very slowly, and the permanganate is not decolorised until the solution has been heated for a considerable time on the water-bath. Little or no dihydroxybehenic acid is formed under these conditions. If more caustic potash is employed, the yield of dihydroxy-acid is greater, being 10 per cent. of the brassidic acid when 50 per cent. of potash is used, and 20 per cent. with 75 per cent. of potash. The dihydroxybehenic acid obtained in this way differs from the isomeride formed by the oxidation of erucic and isoerucic acids. It is insoluble in water, and dissolves more readily in alcohol than in ether. From ethereal solution, it crystallises in microscopic plates, which melt in a capillary tube at 99—100°, solidifying again at 88°. The silver salt is a white, insoluble precipitate. J. W.

Structure of Oleïc, Erucic, and isomeric acids. By A. SAYTZEFF (*J. Russ. Chem. Soc.*, **24**, 504—508).—The following tables of melting points show the correspondence of the oleïc with the erucic series of isomeric acids.

	M. p.	M. p. of dihydroxy-acid.
Oleïc	14°	137°
Iso-oleic....	45°	79°
Elaïdic	52°	100°

	M. p.	M. p. of dihydroxy-acid.
Erucic.....	34°	133°
Iso-erucic...	55°	88°
Brassidic ...	65°	100°

The author considers oleïc and elaïdic acids to be geometrically isomeric, whilst iso-oleïc acid is a structural isomeride. These relations are expressed by the formulæ

$$\begin{array}{l} CH_3\cdot[CH_2]_{13}\cdot C\cdot H \\ \qquad\qquad \| \\ \qquad\quad H\cdot C\cdot CH_2\cdot COOH \end{array} \quad \text{and} \quad \begin{array}{l} H\cdot C\cdot[CH_2]_{13}\cdot CH_3 \\ \qquad\quad \| \\ \qquad\quad H\cdot C\cdot CH_2\cdot COOH \end{array}.$$

Oleïc acid. Elaïdic acid.

Iso-oleïc acid should also exist in two geometrically isomeric forms, namely

$$\begin{array}{l} CH_3\cdot[CH_2]_{14}\cdot C\cdot H \\ \qquad\qquad \| \\ \qquad\quad H\cdot C\cdot COOH \end{array} \quad \text{and} \quad \begin{array}{l} H\cdot C[CH_2]_{14}\cdot CH_3 \\ \qquad\quad \| \\ \qquad\quad H\cdot C\cdot COOH \end{array},$$

but attempts to prepare them have hitherto been attended with no positive results.

A similar set of formulæ may be attributed to the erucic series.

J. W.

Oxidation and Derivatives of Erucic acid. By M. FILETI (*J. pr. Chem.* [2], **48**, 72—74).—When erucic acid is warmed at 70° with nitric acid of sp. gr. 1·48, nonylic (pelargonic) acid is obtained, together with a small quantity of a nitrogenous *compound*, $C_9H_{18}N_2O_4$ (compare Grossmann, this vol., i, 305). Brassylic acid, to which the author attributes the formula $C_{13}H_{24}O_4$, is also a product of the oxidation of erucic acid; it crystallises in prismatic needles, and melts at 114°; the *methylic* salt melts at 36° and boils at 326—328°. Arachic acid is also formed.

By the action of sulphuric acid on chloro- and bromo-brassidic acids, an oxybehenic acid, melting at 83°, was obtained; its sodium salt is very slightly soluble in cold water, and its methylic salt melts at 57—58°.

A. G. B.

Constitution of Behenolic acid. By J. BARUCH (*Ber.*, **26**, 1867—1872; see also this vol., 393).—The reactions of behenolic acid are explained, if it has the constitution $C_8H_{17}\cdot C{:}C\cdot[CH_2]_{11}\cdot COOH$. Thus the oxime of hydroxybrassidic acid, when treated with concentrated sulphuric acid, is converted into pelargonylaminotriskaidecanic acid, $C_8H_{17}\cdot CO\cdot NH\cdot[CH_2]_{12}\cdot COOH$, which splits up into pelargonic acid and amidotriskaidecanic acid (this vol., i, 305).

Pelargonylamidotriskaidecanic acid is decomposed into its two constituents by heating with fuming hydrochloric acid at 230—250°

for 3—4 hours. The pelargonic acid, which is insoluble in water, is best purified by steam distillation. It yields a *barium* salt, which crystallises in lustrous leaflets.

Amidotriskaidecanic hydrochloride, $HCl,NH_2\cdot[CH_2]_{12}COOH$, melts at 132°, and is soluble in water. The *free acid* is a white, crystalline powder, and melts at 163°. The *barium*, *calcium*, and *silver salts* are sparingly soluble. The *ethyl* salt melts at 73°, and is strongly alkaline. The *hydrochloride* of the *ethyl salt* crystallises in beautiful, white needles, and melts at 145°.

Oxybrassidic hydrazide, $N_2\cdot[C(C_8H_{17})\cdot[CH_2]_{12}\cdot COOH]_2$, is obtained by heating an alcoholic solution of oxybrassidic acid, hydrazine sulphate, and sodium hydroxide on the water bath for two hours. It melts at 56°. E. C. R.

Some Derivatives of Pyruvic acid. By L. Simon (*Bull. Soc. Chim.* [3], **9**, 111—112).—Pyruvic acid, hitherto known only as a liquid, has been obtained as a nearly colourless solid, melting at 9°; its index of refraction agrees with the theoretical for CMeO·COOH. The following heats of solution, &c., were observed:—$C_3H_4O_4$ + Aq = 4·4, + NaOHAq = 11·0, + KOH = 10·9, + $\frac{1}{2}$Ba(OH)$_2$ = 12·5 Cal. When oxidised by very dilute alkaline permanganate, it yields acetic acid only. With aniline, ethyl pyruvate gives two yellow, crystalline substances, melting at 144° and 250°, neither of which, consequently, is pyruvic anilide (m. p. 104°). C. F. B.

Ethylic Pyruvate, and the Product of its Condensation by Hydrogen Chloride. By P. Genvresse (*Bull. Soc. Chim.* [3], **9**, 377—380).—Pure ethylic pyruvate was prepared by saturating pyruvic acid in twice its weight of absolute alcohol with dry hydrogen chloride at the temperature of a freezing mixture, and fractionating after 24 hours; it boils without appreciable decomposition at 144°; when treated in ethereal solution with dry ammonia at 18°, it yields a crystalline product, which is unstable, and dissolves freely in water, but only sparingly in ether or alcohol.

The *ethylic salt*, COOEt·CMe:CH·CO·COOEt, is prepared by saturating ethylic pyruvate with hydrogen chloride at the temperature of a mixture of ice and salt, and distilling in a vacuum after 50 days. It is a pale rose-coloured liquid boiling at 170—172° at 20 mm. pressure, without decomposition, and at about 225° at the ordinary pressure, with slight decomposition; it dissolves in alcohol, but not in water, by which it is not decomposed even at the boiling point; its specific gravity is 1·161. The corresponding *acid*, COOH·CMe:CH·CO·COOH, could only be obtained as a syrup. The *normal silver salt* is thrown down as a white precipitate on the addition of silver nitrate to a neutralised solution of the acid; the *normal copper salt*, with 2·5H$_2$O, is a bluish-green powder which is slowly deposited from a mixture of a solution of the neutralised acid with cupric acetate. A. G. B.

Some new Complex Oxalates. By F. Kehrmann and N. Pickersgill (*Zeit. anorg. Chem.*, **4**, 133—137).—Oxalates containing

three metals have been prepared, in the first instance by the action of sodium (or barium or strontium) chloride on double oxalates of potassium with other metals, and subsequently often by crystallising a mixture of the three simple oxalates in the required proportions. They all crystallise in the regular system, some as octahedra with rhombic dodecahedron faces also present, others as triakis tetrahedra, the hemihedral form of the ikositetrahedron. The following have been prepared and analysed: $K_3NaFe(C_2O_4)_3$, green octahedra; $KNa_2Al(C_2O_4)_2 + 4H_2O$, triakis tetrahedra; $KNa_2Cr(C_2O_4)_3 + 4H_2O$, dark-coloured triakis tetrahedra; $KNa_2Co(C_2O_4)_3 + 4H_2O$, dark-green triakis tetrahedra.

Potassium cobalt oxalate and barium chloride give *barium cobalt oxalate*, $Ba_3Co_2(C_2O_4)_6 + 12H_2O$, as tiny, green needles. *Potassium aluminium oxalate*, $K_3Al(C_2O_4)_3 + 3H_2O$, forms colourless monosymmetric prisms. C. F. B.

Dimolecular Propionic Cyanide. Ethyltartronic acid. By K. Brunner (*Monatsh.*, **14**, 120—130).—*Dimolecular propionic cyanide*, $C_5H_{10}N_2O_2$ (compare Claisen and Moritz, Abstr., 1881, 154), has been obtained crystallised in the following manner:—Propionic anhydride (20 grams) is dissolved in dry ether (100 c.c.) and powdered potassium cyanide (10 grams) added to the cooled mixture, which is then shaken for three days. More ether (50 c.c.) is added, the mixture cooled and saturated with gaseous hydrogen chloride, and the ethereal layer then poured off through a filter and allowed to evaporate. The crystals which separate are recrystallised from ether, dried on a porous plate, and recrystallised from alcohol; they are then colourless. The substance has an odour of leeks, melts at 58°, and boils at 227—228° (uncorr.) under 740 mm. pressure. With potash, it yields ammonia, hydrogen cyanide, and propionic acid; with phenylhydrazine, propionylphenylhydrazine, $N_2H_2Ph{\cdot}CEtO$; with hydrochloric acid, ethyltartronic acid (in addition to propionic acid and ammonia?). This acid, $C_5H_8O_5 + H_2O$ (compare Guthzeit, Abstr., 1882, 39), crystallises in tables consisting of two interpenetrating triclinic twins, melts at 64—70°, and when anhydrous at 115—116° with decomposition; the *barium salt*, $C_5H_6O_5Ba + 2H_2O$ (the last $\frac{1}{2}H_2O$ is lost only at 180°), and the *silver salt*, $C_5H_6O_5Ag_2$, were prepared and analysed. When distilled, the acid loses carbonic anhydride and forms α-hydroxybutyric acid. Its formation from dipropionic dicyanide is analogous to that of isomalic acid from diacetyl dicyanide.

C. F. B

The Formula of ordinary Tartaric acid. By A. Colson (*Bull. Soc. Chim.* [3], **9**, 87—90).—A reply to Friedel (this vol., i, 195) and Le Bel, containing also an allusion to Guye's conception of the "product of asymmetry." C. F. B.

Action of Thionyl Chloride on Acid Amides. By A. Michaelis and H. Siebert (*Annalen*, **274**, 312—315).—The authors find that the acid amides, when treated with thionyl chloride, do not yield thionyl derivatives, in a manner similar to the amines, but that this reagent acts on the amides as a dehydrating agent merely, the corresponding

nitrile being formed together with sulphurous anhydride and hydrogen chloride. The reaction is a general one, and has been applied in the cases of acetamide, propionamide, benzamide, and metanitrobenzamide; it is of importance as a means of preparing the nitriles inasmuch as none but gaseous bye-products are formed.

Metamidobenzamide reacts with thionyl chloride forming a colouring matter which appears to be related to those obtained by warming aromatic primary amines with thionyl chloride. A. R. L.

Dipropylamidoacetic acid. By F. Chancel (*Bull. Soc. Chim.* [3], **9**, 234—236).—When dipropylamine (3 mols.) is dissolved in alcohol and heated in a sealed tube at 100—110° for 12 hours with bromacetic acid (1 mol.), *dipropylamidoacetic* acid, $CH_2{\cdot}NPr_2{\cdot}COOH$, is obtained; the *aurochloride* melts at 127°, and the copper salt crystallises with 1 mol. H_2O. A. R. L.

Tripropylamidoacetic acid. By F. Chancel (*Bull. Soc. Chim.* [3], **9**, 236—238).—When dry tripropylamine and ethylic chloracetate are heated together on the water-bath, a syrupy mass consisting of ethylic chloracetate and the *chloride* of *ethylic tripropylamidoacetate* separates at the end of 30 hours. The latter is dissolved in alcohol and converted into the *platinochloride* by the addition of platinic chloride; this compound on decomposition with hydrogen chloride yields the anhydro-compound $CH_2<\begin{matrix}NPr\\CO\end{matrix}>O$; the *hydrochloride* and other derivatives were prepared. A. R. L.

Oxalyl Derivatives. By T. Decev (*J. pr. Chem.* [2], **48**, 78—80).—*Oxamic acid phenylhydrazine*, $NH_2{\cdot}CO{\cdot}CO{\cdot}N_2H_2Ph$, is obtained by the action of ammonia on ethylic oxalylphenylhydrazine (Abstr., 1887, 138); it crystallises in silky laminæ, and melts at 233°. The *methyl* derivative, $NHMe{\cdot}CO{\cdot}CON_2H_2Ph$, crystallises in silvery prisms, and melts at 186°; the *phenyl* derivative melts at 235°. An *acetyl* derivative melts at 224°.

The *phenylhydrazines* of *oxaluric* and *thio-oxaluric* acids, obtained by the action of carbamide and thiocarbamide on ethylic oxalylphenylhydrazine, crystallise in prisms and needles, and melt at 223° and 175° respectively. Ethylic chlorocarbonate forms an oily product with ethylic oxalylphenylhydrazine; this reacts with ammonia to form the *amide*, $NH_2{\cdot}CO{\cdot}CO{\cdot}N_2HPh{\cdot}COOEt$, which melts at 236°, and the *compound* $NH_2{\cdot}CO{\cdot}CO{\cdot}N_2HPh{\cdot}CO{\cdot}NH_2$, which crystallises in laminæ, and melts above 300°. A. G. B.

Action of Ammonia on Mesiten Lactone and its Derivatives. By W. Kerp (*Annalen*, **274**, 267—284).—Anschütz, Bendix, and Kerp (Abstr., 1891, 173) obtained a compound $C_{10}H_{18}N_2O_4$ by passing ammonia into an alcoholic solution of ethylic isodehydracetate; when this is treated with water, it is converted into the so-called basic ammonium salt of ethylic hydroxymesitencarboxylate described by Hantzsch (*Annalen*, **222**, 1). The author regards the last-named compound, however, as the hydrate of ethylic ammonium mesiten-

carbamate, $COOEt\cdot C<\begin{matrix}CMe{:}CH\\CMe-O\end{matrix}>C(NH_2)\cdot ONH_4 + H_2O$, and the following experiments lend support to this hypothesis. Analyses of the *lead* salts of both the methylic and ethylic compounds show that they have the compositions

$$(C_8H_9MeNO_4)_2Pb + H_2O \text{ and } (C_8H_9EtNO_4)_2Pb + H_2O$$

respectively, and are thus derived from the ammonium salts by displacement of NH_4 by Pb. The *cadmium* salt of the methylic compound crystallises with $3H_2O$.

Methylic mesitencarbamate, $COOMe\cdot C<\begin{matrix}CMe{:}CH\\CMe-O\end{matrix}>C(NH_2)\cdot OH$, is obtained by suspending the lead salt in ether and passing in a current of hydrogen sulphide; it crystallises in small, transparent needles, commences to evolve ammonia at 80°, and melts at 92° with decomposition, yielding methylic isodehydracetate. *Ethylic mesitencarbamate* melts at 82° with decomposition. Whereas aqueous hydrochloric acid converts alkylic mesitencarbamates into the corresponding alkylic isodehydracetates, alcoholic hydrogen chloride converts them into the lactams (alkylic oxylutidinecarboxylates).

When treated with hydrochloric acid, the alkylic ammonium mesitencarbamates yield hydroxymesitencarboxylates,

$$COOR\cdot C(CMe\cdot OH)\cdot CMe{:}CH\cdot COOH,$$

and are regenerated when the latter are treated with ammonia.

When bromomesitenlactone (m. p. 106—107°) is heated at 100° with aqueous ammonia, *bromo-ψ-lutidostyril*, C_7H_8BrNO, is obtained; this melts at 186—187°, dissolves sparingly in water, the solution having a faint alkaline reaction, and, on bromination, yields a *dibromo*-derivative melting at 235° with decomposition.

The *lactam* (*ethylic bromhydroxylutidinecarboxylate*), $C_{10}H_{12}BrNO_3$, is obtained by passing dry ammonia into ethylic isodehydracetate at 100°, or by brominating ethylic hydroxylutidinecarboxylate; it melts at 157°. When carefully dried ammonia is passed into an alcoholic ethereal solution of ethylic bromisodehydracetate, the *compound* $COOEt\cdot C<\begin{matrix}CMe{:}CBr\\CMe-O\end{matrix}>C(NH_2)\cdot ONH_4$ is formed; it is much more stable than the non-brominated compound (see above), melts at 122° with decomposition, and forms an *anhydrous lead salt*,

$$(C_{10}H_{12}BrO_4N)_2Pb.$$

Other instances are on record of the formation of salts by the addition of a base to a lactone; thus Perkin (this Journal, 1868, 191) and Williamson (*ibid.*, 1875, 850) show that coumarin forms additive compounds with alkalis capable of being reconverted into coumarin by acids. A. R. L.

Adipin Ketone. By W. Hentzschel and J. Wislicenus (*Annalen*, 275, 312—317).—When anhydrous calcium adipate is distilled, *adipin ketone*, $CO<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}$, passes over between 128° and 130°; it may be purified by conversion into its compound with hydrogen sodium

sulphite; it is a mobile liquid, having the odour of peppermint; it boils at 130—130·5° (corr.), has a sp. gr. at 21·5°/4° = 0·9416, and is sparingly soluble in water. From the higher boiling portion of the above crude distillate, a *compound*, $C_{10}H_{14}O$, can be isolated; this is a bluish oil, which boils at 139—141° (30 mm.) and becomes brownish-yellow if allowed to remain exposed to the air. *Adipinketoxime*, $C_5H_9{\cdot}NOH$, forms long, glittering, friable prisms, melts at 56·5°, boils at 120—121° under a pressure of 45 mm., and at 196—196·5° under 756 mm. pressure; it is decomposed into the ketone when warmed with dilute sulphuric acid.

When adipin ketone is gradually added to warmed nitric acid of sp. gr. 1·2, it yields glutaric acid and a little succinic acid.

A. R. L.

Adipin Ketone from Wood Oil. By W. Hentzschel (*Annalen*, **275**, 318—322).—A ketone-like compound was isolated by Claisen (*Ber.*, **8**, 1258) and by Pinner (*Ber.*, **15**, 594) from the higher boiling fraction obtained in the rectification of wood spirit. Some of this substance boiling between 120° and 140° was shaken with sodium hydrogen sulphite, and the crystalline compound decomposed with soda, when adipin ketone (see preceding abstract) was obtained.

A. R. L.

Pentamethylenic Alcohol and its Derivatives. By J. Wislicenus and W. Hentzschel (*Annalen*, **275**, 322—330).—When adipin ketone is mixed with its own volume of ether, poured into an equal volume of water, and treated with sodium in a reflux apparatus, *pentamethylenic alcohol*, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}OH$, is obtained. It is a colourless oil, very slightly soluble in water, and has the odour of amylic alcohol; its sp. gr. at 21·5°/4° is 0·9395, and it boils at 139°; on oxidation with dilute nitric acid, it yields glutaric and succinic acids. The *iodide*, C_5H_9I, boils at 166—167° (corr.) under a pressure of 754 mm., and has a sp. gr. at 22°/4° = 1·6945. The *bromide*, C_5H_9Br, boils at 136—138°, and has a sp. gr. at 22°(?)/4° = 1·3720. The *amine*, $C_5H_9{\cdot}NH_2$, obtained by reducing the ketoxime (preceding abstract) with sodium and alcohol, is a colourless liquid having a fishy, ammoniacal odour; it boils at 106—108°, fumes in contact with carbonic anhydride, and combines with water with development of heat. The *hydrochloride* crystallises in needles, and is very hygroscopic; the *sulphate* forms silky plates.

Pentamethylene, $CH_2\!<\!\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}$, is obtained by reducing an alcoholic solution of pentamethylenic iodide with zinc and hydrochloric acid. It boils at 50·25—50·75°, has a sp. gr. at 20·5°/4° = 0·7506, and a refractive index at 20·5° = 1·4039, whence its molecular refraction $m\frac{n-1}{d}$ = 37·667 or $M\frac{n^2-1}{(n^3+2)d}$ = 22·799, which fully establishes its cycloïd nature. It behaves as a saturated compound towards bromine, and the halogen is absorbed with the evolution of hydrogen bromide in direct sunlight. Bromine acts slowly on it in the dark at 100°; but at 128—130°, when separation of carbon takes place, the

product consists of unaltered hydrocarbon and pentamethylenic bromide. A. R. L.

Pentamethenylene and its Dibromide. By C. Gärtner (*Annalen*, **275**, 331—332).—Pentamethenylene, $CH_2<\begin{matrix}CH_2\cdot CH\\ \|\\ CH_2\cdot CH\end{matrix}$, is obtained by warming iodopentamethylene (preceding abstract) with alcoholic potash. Almost the whole of the product passes over at 45°. It forms a *dibromide*, $C_5H_8Br_2$, which is a yellowish oil boiling at 105—105·5° (45 mm.). A. R. L.

Pentamethylenecarboxylic acid. By C. Gärtner (*Annalen*, **275**, 333—341).—When adipin ketone (this vol., i, 555) is dissolved in ether, poured upon pulverised potassium cyanide, and concentrated hydrochloric acid added, with cooling, *α-hydroxypentamethylenecarboxylic acid*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot COOH$, is obtained. It crystallises from water in small, colourless needles, and melts at 103°. The *calcium* salt crystallises with $6H_2O$, the *silver* salt is anhydrous, and the *zinc* salt crystallises with $2H_2O$.

When iodopentamethylene is dissolved in 80 per cent. alcohol (3 parts) and heated at 200° in a sealed tube with a slight excess of pulverised potassium cyanide, *pentamethylenic nitrile*,

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CN,$$

boiling at 170—171°, is the chief product. It is converted into the corresponding *carboxylic acid*, $C_5H_9\cdot COOH$, when heated on the water-bath with concentrated hydrochloric acid for eight hours; the yield is small. The acid has an unpleasant odour; it boils at 214—215°, solidifies at −7°, and melts at between −4° and −3°. It is also formed by heating α-hydroxypentamethylenecarboxylic acid with hydriodic acid and phosphorus at 190—195° in a sealed tube for five hours. The *calcium* salt crystallises with $5H_2O$, the *barium* salt with $1H_2O$, and the *silver* salt is anhydrous and fairly stable towards light. When α-hydroxypentamethylenecarboxylic acid is heated on the water-bath with hydriodic acid and phosphorus, a small quantity of an *acid*, C_6H_8O, is formed, the nature of which has not yet been determined; it melts at 120°. A. R. L.

Constitution of Suberone and of the Closed-chain Ketones of Pimelic and Azelaïc acids. By H. Mager (*Annalen*, **275**, 356—366).—The best yield of suberone is obtained by distilling calcium suberate (15 grams at most). The α-pimelic acid, which is obtained by the oxidation of suberone (Schorlemmer and Dale, this Journal, 1874, 934), is shown to be identical with that prepared by W. H. Perkin, jun. (*Ber.*, **18**, 3249) from ethylic malonate and trimethylene dibromide; so that there is no doubt that suberone has the formula assigned to it by Schorlemmer and Dale.

When dehydrated calcium pimelate is distilled, a closed-chain

Ketone, $C_8H_{10}O$, is obtained; it is a colourless oil having the odour of peppermint, boils at 152—155°, and yields adipic acid on oxidation with nitric acid.

Schorlemmer and Dale (*loc. cit.*) obtained normal heptane, together with an oil having the odour of suberone, by the distillation of anhydrous calcium azelaïnate. The author has repeated this experiment, and obtained normal heptane, together with a *ketone*, $C_8H_{14}O$, having a peppermint-like odour, and boiling at 90—91° (23 mm.); on oxidation with potassium permanganate, it gives a bibasic hydroxy-acid, $C_8H_{14}O_5$, melting at about 100°. A. R. L.

Constituents of Wood Oil. By E. Looft (*Annalen*, **275**, 366—382).—A quantity of wood oil was fractionally distilled, and the two principal fractions boiling at 120—140° and 160—180° examined as follows.

The fraction boiling at 120—140° was shaken with a concentrated solution of hydrogen sodium sulphite, and, after collecting the crystals of the sulphite compound of adipin ketone, the filtrate was mixed with a fresh quantity of the salt solution, when it separated into an oily and an aqueous layer. The former boiled at 129—132°, and consisted chiefly of isoamylic alcohol, but after re-fractionation a little pyridine was isolated from the fraction of lower boiling point; the portion boiling at about 140° was soluble in mineral acids, and consisted, therefore, probably of methyl-pyridines.

The chief portion of the fraction boiling at 160—180° consisted of the *ketone* C_6H_8O, a translucent oil of aromatic odour boiling at 157°; it had a sp. gr. of 0·98075 at 16°, and a refractive index of 1·4762 at 15°. The *oxime*, $C_6H_8{\cdot}NOH$, crystallises in nacreous plates, melts at 128°, and forms a dibromo-additive compound melting at 99°. The ketone yields acetic and succinic acids on oxidation with potassium permanganate. The only formula which is in accord with these facts is the following, $CH_2<\begin{matrix}CH_2{\cdot}CO\\ |\\ CH_2{\cdot}CMe\end{matrix}$. When the ketone is shaken with hydrogen sodium sulphite solution, a thick magma of crystals of the *sulphite* compound is formed; dissolution subsequently ensues, however, with rise of temperature, and when the solution is concentrated, sulphurous anhydride is evolved, and, on cooling, large, flat crystals separate out of the composition $C_{12}H_{18}S_2O_8Na_2 + H_2O$. When barium chloride is added to a solution of this salt, the *barium* salt, $C_{12}H_{18}S_2O_8Ba + 3H_2O$, is obtained; the *silver* salt is readily soluble in hot water, and fairly stable towards light. The acid has not yet been prepared, and experiments on its constitution are in progress. A. R. L.

Imido-derivatives of Chlorinated Diketopentene. By T. Zincke and O. Fuchs (*Ber.*, **26**, 1666—1681).—The chlorinated δ-ketonic acids obtained from the ketochlorides of resorcinol and orcinol when treated with ammonia yield imidoketones with elimination of 1 mol. of carbonic anhydride and 3 mols. of hydrogen chloride (this vol., i, 259). Those compounds are obtained by treating the

finely-divided ketonic acids, either suspended in water or dissolved in sodium acetate, with an excess of dilute ammonia, keeping the mixture well cooled with ice.

Dichlorimidoketopentene, $\begin{matrix}CH\cdot C(NH)\\ \|\\ CCl\text{——}CO\end{matrix}>CHCl$, is obtained from the acid $CHCl_2\cdot CO\cdot CCl{:}CH\cdot CCl_2\cdot COOH$. It crystallises in long, white, interlacing needles, melts at 174°, sublimes at a lower temperature, and yields an easily soluble sodium salt. The *imidochloride*,

$$CHCl_2\cdot CO\cdot CCl{:}CH\cdot CCl{:}NH,$$

is obtained by treating it in chloroform solution with excess of chlorine. It crystallises in colourless prisms, melts at 130°, is insoluble in water, hydrochloric acid, and soda, and is easily converted into the amide and amidine. The *amide*, $CHCl_2\cdot CO\cdot CCl\cdot CH\cdot CO\cdot NH_2$, is obtained by treating the imidochloride with sodium hydroxide, adding hydrochloric acid, and extracting with ether. It may also be obtained by saturating with chlorine the acetic acid solution of the imidoketone. It crystallises in beautiful, colourless prisms or radiating needles, melts at 167—168°, dissolves in cold sodium hydroxide without decomposition, and is converted into the corresponding acid when heated with hydrochloric acid at 100°. The *amidine*,

$$CHCl_2\cdot CO\cdot CCl{:}CH\cdot C(NH)\cdot NH_2,$$

is obtained by dissolving the imidochloride in alcoholic ammonia, and evaporating to dryness on the water-bath. It crystallises in colourless, radiating needles, melts at 143—144°, and has basic properties.

Trichlorimidoketopentene, $\begin{matrix}CH\cdot C(NH)\\ \|\\ CCl\text{——}CO\end{matrix}>CCl_2$, obtained from the acid $CCl_3\cdot CO\cdot CCl{:}CH\cdot CCl_2\cdot COOH$, crystallises in long, white needles, melts at 207°, and yields an easily soluble sodium salt which crystallises in long, slender needles. An acetyl derivative could not be obtained. Methylic iodide is without action on the compound. When treated with sodium hydroxide, it is decomposed with evolution of ammonia; ammonia is also formed when it is treated with sodium amalgam. The *imidochloride*, $CCl_3\cdot CO\cdot CCl{:}CH\cdot CCl{:}NH$, is obtained by treating it, dissolved in acetic acid, with excess of chlorine. It crystallises in beautiful, nacreous leaflets or tablets, melts at 141—142°, and is decomposed when heated with water. The *amide*, $CCl_3\cdot CO\cdot CCl{:}CH\cdot CO\cdot NH_2$, crystallises in short spears or large, colourless prisms, melts at 107—108°, and is soluble in hot water and dilute hydrochloric acid. When heated with concentrated hydrochloric acid in a sealed tube at 100°, it is converted into trichloracetyl-β-chloracrylic acid, $CCl_3\cdot CO\cdot CCl{:}CH\cdot COOH$, which melts at 126° (this vol., p. 317).

Tetrachlorimidoketopentene, $\begin{matrix}CCl\cdot C(NH)\\ \|\\ CCl\text{——}CO\end{matrix}>CCl_2$, is obtained from the acid $CCl_3\cdot CO\cdot CCl{:}CCl\cdot CCl_2\cdot COOH$. The yield is not good, as a second reaction takes place with evolution of chloroform, and formation of a compound having the composition $C_3Cl_4O_2NH$, and melting at 80°. The tetrachlorimidoketone is also obtained by heating the amide $CHCl_2\cdot CO\cdot CCl{:}CCl\cdot CONH_2$ with concen-

trated sulphuric acid. It crystallises in long, colourless, felted needles, melts at 203°, and gives a sodium salt which crystallises in beautiful, iridescent leaflets, effloresces on exposure to air, and is decomposed by boiling with water or alcohol. When reduced with hydrogen iodide or sodium amalgam, ammonia is formed. When reduced with sodium in alcoholic solution, a base is obtained which is probably amidopentamethylene. The *imidochloride*,

$$CCl_3{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CN,HCl,$$

crystallises in radiating prisms, and melts at 111°. The amide has already been described (Abstr., 1892, 1186). It melts at 145—146°. The acid obtained from it by heating with hydrochloric acid melts at 85—86° when dry, and at 51—52° when hydrated.

Trichlorimidoketomethylpentene, $\begin{matrix} CMe{\cdot}C(NH) \\ \| \\ CCl\text{---}CO \end{matrix}>CCl_2$, has already been described (this vol., i, 259). It melts at 187·5°. The *imidochloride*, $CCl_3{\cdot}CO\ CCl{:}CMe{\cdot}CCl{:}NH$, crystallises in beautiful, colourless prisms, and melts at 110°. The *amide*, $CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}CO{\cdot}NH_2$, crystallises in white, radiating needles or long leaflets, melts at 117—118°, and when heated with concentrated hydrochloric acid at 150° is converted into the acid $CCl_3{\cdot}CO{\cdot}CCl{:}CMe{\cdot}COOH$, which is identical with that obtained by the oxidation of the ketonic acid from pentachlororcinol.

Dichloracetyl-β-chloracrylic acid, $CHCl_2{\cdot}CO{\cdot}CCl{:}CH{\cdot}COOH$, is obtained from the above trichlorimidoketopentene by heating it with concentrated hydrochloric acid at 100°. It crystallises in concentric prisms or tablets, melts at 106—107°, and, when treated with hypochlorous acid, is easily converted into the acid

$$CCl_3{\cdot}CO{\cdot}CCl{:}CH{\cdot}COOH.$$

Dichloracetyldichloracrylic acid, $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}COOH$, is obtained from tetrachlorimidoketopentene by heating it with hydrochloric acid at 150°, but can be more easily prepared by heating the amide $C_5Cl_4H_3NO_2$ (Abstr., 1891, 689) with concentrated hydrochloric acid. It crystallises in colourless prisms, and melts at 71°.

Dichloracetylchloromethylacrylic acid, $CHCl_2{\cdot}CO{\cdot}CCl{\cdot}CMe{\cdot}COOH$, crystallises in short, colourless needles and prisms, and melts at 105—106°. When treated with dilute bleaching powder solution, it yields the acid $CCl_2{\cdot}CO{\cdot}CCl{:}CMe{\cdot}COOH$ (this vol., i, 317).

E. C. R.

Action of Nascent Bromine on some Benzene Derivatives.—By W. Vaubel (*J. pr. Chem.* [2], **48**, 75—78).—This investigation was conducted by adding sulphuric acid and potassium bromide to an aqueous solution (where possible) of the benzene derivative to be investigated, and pouring into the mixture an aqueous solution of the calculated quantity of potassium bromate. The following general results were noted: the groups OH and NH_2 favour the entry of bromine into the ortho- and para-positions; two of these groups in the meta-position to each other will both influence the bromine substitution in this sense, but they militate against it when they are in

the ortho- and para-positions relatively to each other. These observations confirm the author's previously expressed opinions with regard to the configuration of benzene (Abstr., 1891, 1343). A. G. B.

Iodoso- and Iodoxy-compounds. By C. Willgerodt (*Ber.*, **26**, 1802—1811).—The first portion of this paper consists of a reply to the criticisms of Askenasy and Mayer (this vol., i, 503), in which the author maintains the correctness of the results he has already published. The second portion gives a further account of the metanitroiodoso- and nitroiodoxy-compounds (compare this vol., i, 256).

The metanitroiodosobenzene already described commences to decompose at a low temperature, and it is the first products of decomposition which are completely split up at 195°. Paranitroiodosobenzene explodes without report at 82—83°, the products formed being paranitroiodobenzene and iodic anhydride. It is also converted by acetic acid into the *acetyl* derivative, which separates as a pale yellow substance if only a small quantity of acetic acid is employed. On boiling with water, it is converted into paranitroiodobenzene and *paranitroiodoxybenzene*, $NO_2 \cdot C_6H_4 \cdot IO_2$, the yield of the latter being small. It crystallises from acetic acid in colourless, transparent, six-sided plates, and explodes at 212—213°.

Orthonitroiodobenzene combines with chlorine in chloroform solution yielding *orthonitrophenyl iodochloride*, $NO_2 \cdot C_6H_4 \cdot ICl_2$, which is a yellow, crystalline mass, and melts at 96° with violent decomposition. It cannot be recrystallised without undergoing change, and is readily converted into *orthonitroiodosobenzene*, $NO_2 \cdot C_6H_4 \cdot IO$, in the usual manner; the latter crystallises in orange-yellow prisms, and decomposes at about 100°, the product being impure orthonitroiodoxybenzene. With acetic acid, it yields an acetate which separates in compact crystals, decomposes at 145° with much frothing, and on exposure to the air again forms orthonitroiodosobenzene. *Orthonitroiodoxybenzene*, $NO_2 \cdot C_6H_4 \cdot IO_2$, obtained from the iodoso-derivative in the usual manner, crystallises from acetic acid in thin, transparent, yellowish tablets, and explodes with a sharp report at about 210°.

H. G C.

Action of Aluminium Chloride on Chlorides and Bromides of Aromatic Radicles. By J. Schramm (*Ber.*, **26**, 1706—1709).—Benzyl chloride yields with aluminium chloride, alone or in carbon bisulphide solution, a substance which, when distilled, decomposes into toluene and anthracene; if benzene is used as a solvent, anthracene and diphenylmethane are formed. α-Chlorethylbenzene, CPhMeHCl, with aluminium chloride in benzene solution at 0°, yields unsymmetrical diphenylethane, ethylbenzene, and symmetrical mesodimethyldihydroanthracene, $C_6H_4 < \begin{matrix} CHMe \\ CHMe \end{matrix} > C_6H_4$, the first being doubtless formed by the combination of benzene with cinnamene, itself obtained from the chlorethylbenzene by loss of hydrogen chloride. The product obtained by chlorinating boiling ethylbenzene (? ω-chlorethylbenzene, $CH_2Ph \cdot CH_2Cl$), if mixed with aluminium chloride at 0°, yields dibenzyl, anthracene, and unsymmetrical diphenylethane; the author asserts that the first two are

formed from $\alpha\omega$-dichlorethylbenzene, the last one from α-chlorethylbenzene, both contained in the crude product of chlorination. $\alpha\omega$-Dibromethylbenzene yields dibenzyl, anthracene, and bromobenzene; the formation of the last compound shows that some of the original substance must have decomposed into bromine and cinnamene. C. F. B.

Some Substituted Benzenoïd Hydrocarbons. By P. Genvresse (*Bull. Soc. Chim.* [3], **9**, 219—227).—The heat of combustion of propylbenzene is at constant volume +1246·9 Cal., at constant pressure +1248·6 Cal. Hence the heat of formation C_9 (diamond) + O_{24} (gas) = C_9H_{12} (liquid) .... +14·1 Cal. Errera, by chlorinating the boiling hydrocarbon, obtained a chloropropylbenzene, which gave allylbenzene when treated with alcoholic potash. The author has subjected the vapour of boiling propylbenzene to the action of a slow current of chlorine in a reflux apparatus, until a thermometer plunged into the vapour indicated a temperature of 200°. The product is a chloropropylbenzene, boiling at 208—210° with slight decomposition; it does not attack the eyes, and its sp. gr. is 1·0687. When heated with a concentrated solution of potassium carbonate in a sealed tube at 180—200° for two days, allylbenzene and a *chloropropylbenzene* boiling at 205—206° is obtained. The latter resists the action of potassium carbonate, but is converted into allylbenzene by alcoholic potash, and yields benzoic acid when boiled with alkaline potassium permanganate. Evidence is, therefore, afforded of the existence in the above product of two chloropropylbenzenes containing chlorine in the side chain.

The heat of combustion of isopropylbenzene at constant volume is +1248 Cal., and at constant pressure +1249·9 Cal., so that its formation from its elements develops +17·2 Cal. When isopropylbenzene is chlorinated in the manner described above, it yields *parachlorisopropylbenzene*, boiling at 204—206° with slight decomposition, and at 125° under a pressure of 20 mm. It attacks the eyes, has a sp. gr. = 1·0782, and gives parachlorobenzoic acid on oxidation with alkaline potassium permanganate.

Diisopropylbenzene (b. p. 203—205°) yields terephthalic acid on oxidation with potassium permanganate, and must, therefore, have its two isopropyl groups in the para-position relatively to each other (Beilstein).

The chief product obtained by treating toluene with propylic bromide and aluminium chloride appears from its behaviour on oxidation to be a mixture of 1 : 3-methylpropylbenzene (1 part) and 1 : 4-methylpropylbenzene (5 parts); but it also contains a smaller quantity of isopropyltoluene (see below). It boils at 178—180°; its heat of combustion at constant volume is 1404·2 cal., and at constant pressure 1406·1 Cal., from which the heat of formation +17·9 Cal. is deduced. A *chloro*-derivative boiling at 218—220° was obtained, which, on heating with potassium carbonate, yielded allyltoluene; a small quantity of substance (probably an isomeride) remains unattacked by the potassium carbonate.

The isopropyltoluene mentioned above is a mixture of the 1 : 4-com-

pound, cymene (5 parts), and the 1 : 3-compound (1 part); it boils at 173°. The heat of combustion at constant volume is +1407·25 Cal., and at constant pressure + 1410·1 Cal., whence its heat of formation is +9·9. A. R. L.

Cinnamene Hydrochloride and Hydrobromide. By J. Schramm (*Ber.*, **26**, 1709—1711).—Reasoning from analogy, one would expect the additive compounds of cinnamene with hydrochloric and hydrobromic acids to have the constitution CPhMeHX. Bernthsen and Bender, however (Abstr., 1883, 70), attribute to the hydrobromide the constitution $CH_2Ph{\cdot}CH_2Br$. The author has reinvestigated the matter, and finds that both the hydrochloride and hydrobromide react as if they possessed the first mentioned formula; when boiled in alcoholic solution with potassium cyanide, and then with potash, they yield the ether CPhMeH·OEt and no hydrocinnamic acid; with sodium they yield dimethyldiphenylethane, and the hydrochloride with aluminium chloride in benzene solution yields unsymmetrical diphenylethane and mesodimethyldihydranthracene (compare preceding abstract). C. F. B.

Homologues of Phenol. By B. Fischer and B. Grützner (*Ber.*, **26**, 1646—1649).—*Tertiary amylphenol*, $OH{\cdot}C_6H_4{\cdot}CMe_2Et$, is obtained by heating phenol with dimethylethylcarbinol and zinc chloride in a reflux apparatus at 180°. It crystallises from light petroleum in long, interlacing needles, melts at 93—94°, boils at 265—267°, is volatile with steam, and has a pleasant aromatic odour resembling that of thymol. The *sodium* salt crystallises in white scales, and absorbs carbonic acid from the air. The *acetyl derivative* is a colourless oil, which boils at 264—266°, and is easily decomposed by sodium hydroxide.

Amylanisoil, $OMe{\cdot}C_6H_4{\cdot}C_5H_{11}$, obtained by heating amylphenol with potassium hydroxide and methylic iodide, is an oil, and boils at 240—241°. E. C. R.

Supposed Formation of Orthocresol from Methylsalicylic acid [COOH : OH : Me = 1 : 2 : 5]. By P. de Chambrier (*Ber.*, **26**, 1692 — 1694). — Methylsalicylic acid [COOH : OH : Me = 1 : 2 : 5], on distillation with lime, yields paracresol, not orthocresol, as stated by O. Jacobson (*Ber.*, **11**, 377), together with a little phenol, the formation of the latter being probably due to oxidation by the lime of a part of the methylsalicylic acid to hydroxyisophthalic acid. Reuter's assertion that dimethylsalicylic acid [COOH : OH : Me : Me = 1 : 2 : 4 : 5], on distillation with lime, yields metaxylenol [Me : Me : OH = 1 : 3 : 4] (*Ber.*, **11**, 30) is also unlikely to be correct. J. B. T.

Hemiacetals derived from Substituted Chloranils. By C. L. Jackson and H. S. Grindley (*Ber.*, **26**, 1631—1633; see also this vol., ii, 322).—When diphenoxydichloroquinone is treated with sodium methoxide, a *derivative* of *dimethoxydichloroquinone*,

$$C_6(OMe)_2Cl_2O_2,2MeOH,$$

is obtained. It is a white substance, and when heated at 170—173°,

is converted into the dimethoxydichloroquinone melting at 141—142°. The same change takes place when the compound is treated with sulphuric or hydrochloric acid, or is boiled with water or dilute alcohol, or when the sodium salt is heated with benzoic chloride or acetic anhydride.

Sodium ethoxide reacts in the same way, and yields a compound of the formula $C_6(OEt)_2Cl_2O_2,2EtOH$, which, when heated at 140—143°, is converted into diethoxydichloroquinone melting at 104—105°.

The authors are studying the action of sodium alkyl oxides on various quinones. E. C. R.

Action of Acid Chlorides on Nitrosodimethylaniline. By P. Ehrlich and G. Cohn (*Ber.*, **26**, 1756—1757).—The authors have found that acid chlorides combine very readily with nitrosodimethylaniline and other nitroso-derivatives, forming additive compounds, the reaction being sufficiently violent to render dilution with benzene advisable.

With benzoic chloride and nitrosodimethylaniline, an almost quantitative yield of the new compound is obtained; it forms a yellowish precipitate, and if quickly dried may be kept for some time. It is precipitated from alcoholic solution on the addition of ether in white, unstable plates, which have the composition $C_{15}H_{13}N_2O_2Cl$, and the substance is therefore formed by the direct union of the two components. Two formulæ are possible for such a product, namely, $NMe_2{\cdot}C_6H_4{\cdot}NCl{\cdot}OBz$ and $NMe_2Cl{\cdot}C_6H_4{\cdot}N{\cdot}OBz$, of which the authors regard the latter as the more probable. The most remarkable property of the new compound is the readiness with which it reacts with bases and phenols, to form colouring matters, even in the cold. When alcoholic solutions of the new compound and of tolylenediamine are mixed, an intense blue coloration is immediately produced, which does not deepen on keeping. H. G. C.

Products of the Action of Aniline on Dibromosuccinic acid. By A. Reissert (*Ber.*, **26**, 1758—1765).—Some years ago the products of the action of aniline on dibromosuccinic acid were examined by the author and Tiemann, who obtained a mixture of two acids having the composition $C_{16}H_{14}N_2O_3$ and $C_{16}H_{12}N_2O_2$, and containing therefore respectively the elements of 1 and 2 mols. of water less than the expected dianilidosuccinic acid. The same compounds were also obtained shortly afterwards by Michael, who regarded them as anilidomaleïnanilic acid and anilidomaleïnanil (Abstr., 1886, 698). As the latter compound has recently been obtained by Bischoff (this vol., i, 55) by the action of phosphorus pentachloride on the dianilide of tartaric acid, it can hardly have the constitution assigned to it by Michael; the author has therefore reinvestigated the subject with the following results.

The substance obtained by boiling dibromosuccinic acid (1 mol.) with 10 times its weight of aniline (6 mols.) consists of the compound $C_{16}H_{12}N_2O_2$, and of the aniline salt of the acid $C_{16}H_{14}N_2O_3$, together with a small quantity of the aniline salt of β-anilidoacrylic acid. If the mixture is boiled with aqueous soda, aniline is liberated, and on

the addition of acetic acid, β-anilidoacrylic acid separates, mixed with some dianilidosuccinic acid, whilst the addition of hydrochloric acid causes a fresh precipitate, consisting chiefly of the dianilido-acid.

β-Anilidoacrylic acid, $NHPh{\cdot}CH{:}CH{\cdot}COOH$, is best obtained pure by recrystallising its sodium salt from 80 per cent. alcohol, acidifying, and extracting with ether. It is a very unstable substance, and cannot be recrystallised; it becomes coloured at 100°, sinters at 150°, and melts with decomposition at 160°. The *sodium* salt crystallises in small, lustrous, indistinct crystals.

Dianilidosuccinic acid may be obtained from the impure product described above by recrystallising the sodium salt from absolute alcohol, and saturating the aqueous solution with hydrogen chloride. The properties observed agree with those described by Gorodetski and Hell (Abstr., 1888, 951).

As already stated, Michael regarded the acid $C_{16}H_{14}N_2O_3$ as anilidomaleïnanilic acid, $COOH{\cdot}C(NHPh){\cdot}C{:}CO{\cdot}NHPh$, but in view of Bischoff's synthesis, this view is no longer tenable, and the author believes that it is an anhydro-compound, having probably the constitution $\begin{matrix}NPh{\cdot}CH{\cdot}COOH\\ |\quad\quad\quad|\\ CO-CH{\cdot}NHPh\end{matrix}$. The second compound, $C_{16}H_{12}N_2O_2$, which Michael believed to be anilidomaleïnanil, is being further investigated by Bischoff, and has therefore not been examined by the author, who, however, proposes to term it for the present *dianilsuccin*.

Dinitrosoanilidosuccinic acid, $C_{16}H_{14}N_2O_4(NO)_2$, is obtained by the careful addition of hydrochloric acid to a solution of sodium nitrite and the sodium salt of the acid, and forms yellow, indistinct crystals; it melts at 142·5°, and shows Liebermann's reaction. On reduction with zinc and acetic acid, it does not yield the corresponding diphenylhydrazidosuccinic acid, as the latter probably at once loses ammonia, forming *diphenylosotriazolidinedicarboxylic acid*,

$$HN<\begin{matrix}NPh{\cdot}CH{\cdot}COOH\\ |\quad\quad\quad|\\ NPh{\cdot}CH{\cdot}COOH\end{matrix};$$

this forms a light, white, amorphous mass, which is decomposed by boiling with water, and melts with much frothing at 95°.

H. G. C.

Action of Paratoluidine on Dibromosuccinic acid: New Derivatives of Dianilidosuccinic acid. By A. Junghahn and A. Reissert (*Ber.*, **26**, 1766—1773; compare preceding abstract).—Paratoluidine acts on dibromosuccinic acid in a very similar manner to aniline, yielding a mixture of different substances. When the product is treated with alkalis, paratoluidine is liberated, and part of the remainder goes into solution; the residue, after repeated crystallisation from alcohol, forms golden-yellow, lustrous plates, and melts at 228°. It has the composition $C_{18}H_{18}N_2O_2$, and corresponds exactly with the indifferent compound obtained from aniline, and may therefore be termed *diparatolilsuccin*. The acid corresponding with anhydrodianilidosuccinic acid could not be obtained pure, as it readily takes up water, forming *diparatoluidosuccinic acid*,

$$C_2H_4(NH{\cdot}C_7H_7)_2(COOH)_2,$$

which may be prepared from the mixture in a similar manner to the corresponding anilido-derivative. It is a crystalline substance, which becomes yellow at 100° and melts at about 200°; the *sodium* salt forms stellate groups of hair-like needles, the *calcium* salt a white, flocculent precipitate, the *copper* salt a grass-green precipitate, and the *ethylic* salt white needles, melting at 169°. The *dinitroso*-derivative, $C_{18}H_{18}N_2O_4(NO)_2$, crystallises in small needles, melts at 125°, and gives Liebermann's reaction.

If the sodium salt of the acid is boiled with acetic anhydride, it is converted into a substance which forms small, prismatic crystals, blackens at 215°, and decomposes completely at 222°. It is derived from the *diacetyldiparatoluidosuccinic acid* first produced, by the loss of 2 mols. H_2O, and is converted into the acid by boiling with 10 per cent. alkali, and adding hydrochloric acid; the latter crystallises with $1H_2O$, in small prisms, becomes yellow at 170°, and decomposes completely at 204°. The *calcium* and *barium* salts also contain $1H_2O$. When the acid is boiled with acetic anhydride, it yields the corresponding anhydride, $C_{22}H_{22}N_2O_5$, a white, crystalline substance, which melts at 232° with evolution of gas and previous darkening.

If the sodium salt of dianilidosuccinic acid is boiled with acetic anhydride, it yields the *diacetyldianilidosuccinic* anhydride, but this compound could in no way be made to yield a substance containing 2 mols. less H_2O than the diacetyldianilidosuccinic acid. The *anhydride* $\begin{matrix}NAcPh\cdot CH\cdot CO\\ NAcPh\cdot CH\cdot CO\end{matrix}>O$ forms white needles, and melts at 192°; the acid itself crystallises in white prisms containing $1H_2O$, and melts at 172—173°. The *silver* salt is a white, flocculent precipitate, and contains no water of crystallisation, whilst the *sodium* and *calcium* salts are crystalline substances, and contain $6H_2O$ and $2H_2O$ respectively. H. G. C.

Electrolytic Reduction of Aromatic Nitro-compounds. By L. GATTERMANN (*Ber.*, **26**, 1844—1856).—The nitro-compound is dissolved in 5 to 10 times its weight of concentrated sulphuric acid, and the cold solution put into a porous cell, which stands in a beaker containing 75—100 per cent. sulphuric acid. The inner cell contains a platinum cathode, and the outer cell a platinum anode. A current of $1\frac{1}{2}$ to 3 ampères at a potential of 5 to 6 volts is used. Heat is evolved during the reaction. The products usually separate as sulphates, either at once or on remaining in a cool place. If the product is very soluble in sulphuric acid, it is precipitated on the addition of water. The following results were obtained.

Nitrobenzene yields paramidophenol sulphate. Orthonitrotoluene yields an amidocresol, which is easily soluble in alkali, and gives a violet coloration with ferric chloride; the author is engaged in the further examination of this compound. Metadinitrobenzene yields orthoparadiamidophenol, which is identical with the compound obtained from orthoparadinitrophenol. Orthoparadinitrotoluene yields *diamidocresol*, $C_6H_2Me(NH_2)_2\cdot OH$ [1 : 4 : 6 : 3]. It crystallises in broad needles, is unstable, and melts at 170° with a brown coloration.

The *sulphate* crystallises in colourless needles, turns brown on exposure to air, and gives an intense violet coloration with ferric chloride, dichromate, nitric acid, and bromine water.

Metanitraniline yields orthoparadiamidophenol. Orthonitroparatoluidine yields the diamidocresol (m. p. 170°) described above, which is also obtained by the electrolytic reduction of paranitroorthotoluidine.

Metanitrobenzoic acid yields amidosalicylic acid [COOH : NH_2 : OH = 1 : 3 : 6]; this crystallises in long, colourless needles, is not altered by exposure to air, and is decomposed by heat into amidophenol and carbonic anhydride. The *sulphate* crystallises in broad, colourless needles.

Metanitroparatoluic acid yields *amidocresotic acid*,

$$[COOH : NH_2 : Me : OH = 1 : 3 : 4 : 6].$$

The *sulphate* crystallises with water in colourless needles which effloresce on exposure to air; it gives a violet coloration with ferric chloride. By displacing the amido-group in amidocresotic acid by chlorine, bromine, and iodine, the following compounds were obtained: *chlorocresotic acid* crystallises in white plates, and melts at 203—204°; *bromocresotic acid* crystallises in silvery leaflets, and melts at 211°; *iodocresotic acid* crystallises in short needles, and melts at 227°.

Nitroterephthalic acid yields the *amidohydroxy-acid*,

$$NH_2 \cdot C_6H_2(COOH)_2 \cdot OH.$$

It separates in beautiful crystals from hot water, gives a reddish-brown coloration with ferric chloride, and when treated with nitrous acid yields a sparingly soluble diazo-compound, which crystallises in short, brownish-red needles.

Nitroisophthalic acid also yields an amidohydroxy-acid, which crystallises with $1H_2O$ in colourless needles, and is dehydrated by heating at 180°.

1 : 4'-Nitronaphthalenesulphonic acid yields a compound which crystallises from water in silvery plates, and reduces ammoniacal silver solution in the cold. It is either an amidonaphtholsulphonic acid or an amidosultone.

Paranitrotoluene behaves in quite a different way from the above compounds, and yields a condensation product which the author believes to be *nitroamidoorthobenzyltoluene*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NO_2$. It forms orange-red crystals, and melts at 119°. The *sulphate* crystallises in beautiful, white needles, which redden on exposure to air. The *acetyl compound*, $NO_2 \cdot C_{14}H_{12} \cdot NHAc$, crystallises in short, yellow needles, and melts at 174°. The *benzoyl compound* crystallises in silky needles, and melts at 185°. The *thiocarbamide*, obtained by warming an alcoholic solution of the base with phenyl isothiocyanate, crystallises in white leaflets, and melts at 167°. The base combines with benzaldehyde to yield a *benzylidene derivative*, $NO_2 \cdot C_{14}H_{12} \cdot N{:}CHPh$, which crystallises in broad, colourless needles, and melts at 194°. The *phenol*, $NO_2 \cdot C_{14}H_{12} \cdot OH$, obtained from the base in the usual way through the diazo-compound, crystallises in yellow needles, and melts at 117°. The *dibromide*, $C_{14}H_{12}N_2O_2Br_2$, crystallises in colour-

less leaflets, and melts at 150°. When the nitroamido-base is reduced with stannous chloride and hydrochloric acid, it yields a *diamine*. The latter boils at 380°, melts at 59—60°, and crystallises in long needles. The *sulphate* crystallises in colourless needles. The *diacetyl derivative*, $C_{14}H_{12}(NHAc)_2$, melts at 220°. The *phenol*, $C_{14}H_{12}(OH)_2$, obtained in the usual way, crystallises in long needles, and melts at 138—139°. E. C. R.

Action of Sodium Sulphite on Salts of Amidophenols. By A. Lumière and A. Seyewitz (*Compt. rend.*, **116**, 1202—1205).—Amidophenols are difficult to isolate from their salts, by reason of the energy with which they absorb oxygen from the air, and this is true also of diamidophenols and triamidophenols. The separation can, however, be effected by means of sodium sulphite, provided that the particular amidophenol is insoluble in a solution of sodium sulphite and is so feebly basic that it will not combine with sulphurous acid.

A concentrated solution of paramidophenol hydrochloride, when treated with a saturated solution of sodium sulphite, yields the base in white, crystalline, nacreous plates which, after being dried at 30—40°, melt at 184°. The reaction is practically quantitative. The product is, however, liable to become slowly black when exposed to the air, but this can be prevented by using for precipitation and the washing of the precipitate a solution of sodium sulphite which is slightly acid to phenolphthaleïn.

Diamidophenol must be precipitated in a saturated solution of sodium sulphite containing some undissolved crystals of the salt and mixed with sufficient sulphurous acid to make it slightly acid to phenolphthaleïn. The hydrochloride is dissolved in 5 parts of this solution and powdered sodium sulphite added until it no longer dissolves; the diamidophenol then gradually separates. It melts at 78—80° and alters very rapidly when exposed to air, but can be kept in flasks filled with sulphurous anhydride. It is somewhat soluble in water, alcohol, and acetone, and slightly soluble in ether, benzene, and chloroform. It dissolves very readily in either acid or alkalis, and all its solutions oxidise when exposed to air. Oxalic acid converts the base into a white powder, insoluble in water and stable when exposed to air. This product is probably diamidophenol oxalate, and it is under investigation.

When a concentrated aqueous solution of triamidophenol hydrochloride is mixed with a saturated solution of sodium sulphite, an abundant, white precipitate is formed, which is very slightly soluble in cold water or in alcohol. This product forms white plates which melt at 120—121° with evolution of sulphurous anhydride. It dissolves in acids with evolution of sulphurous anhydride, and it also dissolves in alkalis. All the solutions oxidise when exposed to air. The compound has the composition $C_6H_3(NH_2)_3{\cdot}OH,H_2SO_3$, and its formation is due to the fact that triamidophenol is a more energetic base than amidophenol or diamidophenol. C. H. B.

Cinnamylamine and its Derivatives. By T. Posner (*Ber.*, **26**, 1856—1865).—*Cinnamylphthalimide*, $CHPh{:}CH{\cdot}CH_2{\cdot}N{\cdot}C_8H_4O_2$, is ob-

tained by heating cinnamyl chloride with potassium phthalimide at 160°. It crystallises in small, white needles, and melts at 153°.

Cinnamylphthalamic acid, $C_9H_9{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is obtained by dissolving the preceding compound in warm potassium hydroxide and precipitating with hydrochloric acid. It melts at 132°. The *silver* salt is a white, flocculent precipitate which turns brown on exposure to light.

Cinnamylamine, $CHPh{:}CH{\cdot}CH_2{\cdot}NH_2$, is obtained, together with phthalic acid and cinnamylphthalimide, by heating the preceding compound with concentrated hydrochloric acid in a reflux apparatus. It is also obtained as hydrochloride, together with di- and tricinnamylamine hydrochlorides, by heating cinnamyl chloride with alcoholic ammonia at 100°. The product is shaken with equal parts of water and ether; the cinnamylamine hydrochloride dissolves in the water; the ether extracts the resinous products and the di- and tristyrylamine hydrochlorides remain undissolved. Cinnamylamine is a colourless, oily liquid, boils at 235—237° under 775 mm. pressure, is sparingly volatile with steam, and has an odour resembling that of benzylamine. It absorbs carbonic anhydride from the air with great readiness. The *hydrochloride* crystallises in white, silky needles, and melts at 210°. The *picrate* melts at 173°. The *platinochloride* melts at 205—207°.

Cinnamylbenzamide, $CHPh{:}CH{\cdot}CH_2NHBz$, crystallises in needles, and melts at 94—95°.

Cinnamylphenylthiocarbamide separates in beautiful, white crystals, and melts at 116—118°.

Cinnamylphenyl-ψ-thiocarbamide, $NHPh{\cdot}C\lessdot^{N—CH_2}_{S{\cdot}CHPh}>CH_2$ or $NHPh{\cdot}C\lessdot^{N{\cdot}CH_2}_{S{\cdot}CH{\cdot}CH_2Ph}$, is obtained by heating the preceding compound with fuming hydrochloric acid at 100° for three hours, and treating the product with alkali. It crystallises in beautiful, colourless prisms, and melts at 205°. The *hydrochloride* and *hydrobromide* do not crystallise, and are insoluble in the presence of the free acid. The *picrate* crystallises in beautiful yellow needles, and melts at 200°. The *platinochloride* is a bright yellow, microcrystalline precipitate, and melts at 182° with decomposition.

Two isomeric *cinnamylphthalimide dibromides*,

$$C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CHBr{\cdot}CHPhBr,$$

are obtained by adding bromine to a well-cooled solution of styrylphthalimide in chloroform. They are separated by fractional crystallisation from ethylic acetate; the less soluble compound crystallises in white needles, and melts at 165°, whilst the more soluble compound forms colourless, nodular aggregates, and melts at 117°.

Dicinnamylamine, $NH(CH_2{\cdot}CH{:}CHPh)_2$, is obtained as described above. It is separated from the tricinnamylamine by means of ethylic acetate, in which it is sparingly soluble. It is a colourless oil, and boils at a very high temperature. The *hydrochloride* crystallises in large, white scales, melts at 223° with a brown coloration, and when heated with amylic nitrite yields a colourless oil. The *picrate* crystallises in long, yellow needles, and melts at 126°.

Tricinnamylamine, $N(CH_2{\cdot}CH{:}CHPh)_3$, forms long, colourless needles, and melts at 89°. The *hydrochloride* melts at 101°. The *methiodide* crystallises in six-sided columns, melts at 129—130°, and colours yellow on exposure to air. The corresponding *chlorine compound* is obtained by treating an alcoholic solution of the iodide with excess of freshly prepared silver chloride. It melts at 166°. The *platinochloride*, $C_{56}H_{60}N_2PtCl_6$, is an insoluble, yellow precipitate, and melts at 195°. E. C. R.

Action of Nitrous acid on Ketoamines. By A. Angeli (*Ber.*, **26**, 1715—1719).—Nitrous acid reacts quite generally with the amido-group, but it seems that the diazo-compound primarily formed is only stable when this group is directly connected with a group of negative character (for example, phenyl), or, as in the case of diazo-compounds of amido-acids, is joined to a carbon atom which is itself joined to a negative group. The ketoamines, containing the group $-CO{\cdot}CH(NH_2)-$, also satisfy this last condition, and we might expect them to behave like the amido-acids, and yield diazo-derivatives. This they actually do; amidoacetophenone hydrochloride, when it is mixed with sodium nitrite in aqueous solution, and acetic acid is added to the cooled mixture, yields *monoketazophenylglyoxal* or *diazoacetophenone*, $CPhO{\cdot}CH{:}N_2$, which forms lustrous, yellow needles melting at 50°; amidocamphor hydrochloride in like manner yields *monoketazocamphorquinone*, $C_8H_{14}\begin{matrix}CO\\|\\C{:}N_2\end{matrix}$; this forms yellow crystals, melts at 74°, and gives with benzaldehyde in toluene solution a substance melting at 170°, probably benzoylcamphor. C. F. B.

Action of Diazobenzeneimide on Methylic Acetylenedicarboxylate. By A. Michael (*J. pr. Chem.* [2], **48**, 94—95).—When these compounds in equivalent proportion are mixed in ether and exposed to sunlight, or heated in a sealed tube, a white *compound*, $C_{12}H_{11}N_3O_4$, which crystallises in needles and melts at 126—127°, is formed. By treating this ethereal salt with alcoholic potash, the corresponding acid was isolated and was found to melt at 149—150° with decomposition. The reaction is comparable with those observed by Buchner (Abstr., 1889, 694; this vol., i, 432) and by v. Pechmann (Abstr., 1891, 1115). A. G. B.

Nitrohydroxy- and Nitroamido-azo-compounds. By E. Täuber (*Ber.*, **26**, 1872—1876).—Nitroamidoazosulphonic acids are easily obtained by heating nitrohydroxyazosulphonic acids with 20—25 per cent. ammonia at 150—160° for 16 hours. The nitrohydroxyazosulphonic acids are obtained by dissolving hydroxyazosulphonic acids in concentrated sulphuric acid, adding the theoretical quantity of potassium nitrate, and then pouring the mixture into water.

The author has prepared the following compounds by this method:—Metanitroparahydroxyazobenzeneparasulphonic acid, metanitroparahydroxyazobenzenemetasulphonic acid, metanitroparamidoazobenzeneparasulphonic acid, metanitroparamidoazobenzenemetasulphonic acid,

and the homologous compounds derived from the toluidinesulphonic acids. E. C. R.

Azo-derivatives of Quinol. By O. N. Witt and E. S. Johnson (*Ber.*, **26**, 1908—1912).—These cannot be prepared directly by the action of a diazo-compound on quinol, because of the reducing power of the latter. If, however, it be converted in the usual way into *benzoylquinol*, $OH\cdot C_6H_4\cdot OBz$ (flat, colourless, glassy needles, melting at 162—163°), this substance, when treated with a diazo-compound, $R\cdot C_6H_4\cdot N_2\cdot Cl$, yields an azo-colouring matter,

$$R\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot OBz,$$

and from this benzoate, by hydrolysis with alcoholic potash, the corresponding azo-derivative, $R\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$, of quinol itself is obtained.

Anilineazoquinol, $N_2Ph\cdot C_6H_3(OH)_2$, forms red needles melting at 145—148°. the *benzoate*, orange-red crystals melting at 110—112°. *Paratoluidineazoquinol*, $C_6H_4Me\cdot N_2\cdot C_6H_3(OH)_2$, forms greenish-black needles, red by transmitted light, melting at 168—170·5°; the *benzoate* lustrous, silky, orange-yellow needles melting at 113—115·5°. *Paranitranilineazoquinol*, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$, forms large, black tables with greenish, adamantine lustre, and decomposes at 185—190°; the *benzoate* forms lustrous, brownish-red needles melting at 195—197°. *Sulphanilic acid azoquinol*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$, was obtained in the form of its *sodium salt*, a reddish-brown, crystalline precipitate; the *sodium* and *barium salts* of the *benzoate* form golden-yellow crystals. C. F. B.

Action of Ethylenic Bromide on Phenylhydrazine. By C. D. Harries (*Ber.*, **26**, 1865—1867).—When phenylhydrazine and ethylenic bromide, dissolved in alcohol, are heated on the water-bath for 10 hours, a crystalline product is obtained which melts at 179—180°, and is a mixture of two isomeric *diethylenetriphenylhydrazines*, $(C_2H_4)_2{:}N\cdot NH\cdot C_6H_3(NHNHPh)_2$.

The less soluble isomeride crystallises in beautiful, long, lustrous prisms, reduces Fehling's solution and silver solution when warmed, and is a weak base. It dissolves in nitric acid with a characteristic deep-blue colour, and, when reduced with zinc dust and hydrochloric acid, yields ammonia and aniline. The *platinochloride* crystallises in thick, dark red prisms.

The more soluble isomeride forms beautiful crystals, melts at 167—168°, and has properties similar to the preceding, but is more soluble.

If the mixture of phenylhydrazine, ethylenic bromide, and alcohol is heated too rapidly or for too long a time, a deep brown solution is obtained which deposits a crystalline compound melting at 179—180°. It forms long, bright-brown spears, and does not give a blue solution with nitric acid. E. C. R.

The so-called Hydrazone of Cyanacetone. By L. Bouveault (*Bull. Soc. Chim.* [3], **9**, 375—377).—Burns (this vol., i, 315) has

described the compound obtained by the action of phenylhydrazine on imidoacetylacetonitrile as cyanacetone hydrazone. The author points out that this compound has none of the properties of a hydrazone, in which respect it resembles the compound which he obtained (Abstr., 1891, 52) when submitting propionylpropionitrile to a similar treatment. He seeks to account for the irregular behaviour of these hydrazones by postulating an intramolecular transposition whereby the hydrazone becomes an amidopyrazole; $N_2HPh{:}CEt{\cdot}CHMe{\cdot}CN$, for example, becoming

$$NPh\begin{cases} N=\!=\!=CEt \\ C(NH_2){:}CMe \end{cases}.$$

If this view be correct, it will be found that these compounds distil unchanged at the ordinary pressure, and that they behave as primary aromatic bases towards nitrous acid, yielding salts of diazo-derivatives. A. G. B.

Stereoisomerism of the Benzhydroxamic acids. By W. Lossen (*Ber.*, **26**, 1818—1819).—A rejoinder to Werner (this vol., i, 510).

The Two Isomeric Benzyl Derivatives of Nitroso-β-benzylhydroxylamine. By R. Lindner (*Annalen*, **275**, 133—144).—The *sodium* salt of nitroso-β-benzylhydroxylamine melts at 233—234° with decomposition, and the *silver* salt melts at 108—109° with decomposition. On benzylating the sodium salt as described by Behrend and König (Abstr., 1891, 1035), the compound melting at 58—59° is obtained, together with oily products and a small quantity of the isomeric compound melting at 73—74°. The latter was obtained by Behrend and König (*loc. cit.*) by the action of nitrous acid on α-dibenzylhydroxylamine. Both compounds have the same molecular weight, give Liebermann's reaction, and are insoluble in alkalis. When an ethereal solution of the compound melting at 73—74° is treated with hydrogen chloride, α-dibenzylhydroxylamine is obtained, whereas the compound melting at 58—59° remains unaltered under these circumstances; when, however, the latter is heated in a sealed tube at 120—130° with hydrochloric acid, β-benzylhydroxylamine, benzyl chloride, and nitrogen are formed. Both compounds give benzylamine and benzylic iodide on reduction with hydriodic acid and phosphorus.

The author concludes from these experiments that the compound melting at 58—59° has the constitution represented by one of the formulæ $\begin{matrix} C_7H_7{\cdot}N \\ | \\ C_7H_7{\cdot}N \end{matrix}\!>\!O$ or $C_7H_7{\cdot}NO{:}N{\cdot}OC_7H_7$, whilst the compound melting at 73—74° is a true nitrosamine. A. R. L.

Paramagenta. By A. Miolati (*Ber.*, **26**, 1788—1790).—Three different views are at present held as to the nature of the change which takes place when pararosaniline is converted into one of its coloured salts. The oldest supposition is that union takes place between the methane carbon atom and one of the nitrogen atoms,

the latter also combining with the acid, the hydrochloride having, for example, the constitution $C(C_6H_4\cdot NH_2)_2<\begin{matrix}C_6H_4\\ |\\ NH,HCl\end{matrix}$. Nietzki, on the other hand, regards the coloured salts as derivatives of substituted quinonimide compounds, and ascribes to the hydrochloride the formula $(C_6H_4\cdot NH_2)_2C{:}C_6H_4{:}NH,HCl$, whilst Rosenstiel and v. Richter suggest that it may be formed by the substitution of chlorine for the hydroxyl group in pararosaniline, as shown by the formula $CCl(C_6H_4\cdot NH_2)_3$.

If the latter supposition is correct, the salt, like other similar tertiary chlorides, must be a non-electrolyte, whereas, if it has either of the first two formulæ, it must conduct electricity in the same manner as the metallic salts. Experiment has shown that a solution of the salt does conduct electricity, its molecular conductivity being about 46·5. Pararosaniline is therefore a stronger base than quinaldine, and its salts undergo electrolytic dissociation in aqueous solution; so that the formula proposed by Rosentiel and v. Richter cannot be correct. Between the other two formulæ this method is unable to decide. H. G. C.

A New Series of Colouring Matters. By A. Trillat (*Compt. rend.*, **116**, 1382—1385).—Formaldehyde reacts readily with aniline, yielding anhydroformaldehydaniline, $C_6H_5N{:}CH_2$ (this vol., i, 439). When paraleucaniline is dissolved in dilute alcohol and treated with formaldehyde, two of the phenyl groups undergo a similar transformation, and the product is a white powder which melts at 198°, turns blue when exposed to air, dissolves in acids, and is decomposed by alkalis. If the reaction takes place in presence of an acid, the change goes no further, but the product is insoluble in acids.

Rosaniline, with formaldehyde, yields a violet colouring matter similar to that obtained by Lauth from rosaniline and acetaldehyde. It dissolves readily in acids, but although the dye resists the action of soap fairly well when applied to fabrics, it is not stable. In order to obtain this product, 50 grams of rosaniline is dissolved in 500 c.c. of water acidified with 25 grams of sulphuric acid, and the warm liquid is mixed with 25 grams of a 40 per cent. solution of formaldehyde. The liquid is then heated until its colour undergoes no further change. The sulphone derivative of rosaniline yields a similar product, which, however, is redder in colour, and stable when exposed to light, but does not resist washing so well.

Safranine readily yields an analogous product when mixed with formaldehyde in presence of an excess of hydrochloric acid. It has the composition $CH_2{:}N\cdot C_6H_3{:}N_2Cl(C_6H_4)_2N{:}CH_2$, forms crystals with a very brilliant metallic lustre, dyes silk, wool, and cotton without a mordant, and the colour resists the action of soap and hot water in a very remarkable manner.

Diamidophenylacridine, $C_{19}H_{15}N_3$, yields an orange derivative, $C_{19}H_{11}N_3(CH_2)_2$, only slightly soluble in acids, and similar to chrysaniline in its tinctorial properties.

Amidoalizarine also reacts with formaldehyde in presence of a

large excess of sulphuric acid, and yields a dye with a somewhat more violet shade.

When chrysoïdine, sulphuric acid, and formaldehyde are heated together on a water-bath, a new colouring matter is obtained which dyes cotton brick-red without a mordant. From analogy, it would seem to have the constitution $C_6H_5N{:}NC_6H_3{:}(N{:}CH_2)_2$.

20 grams of Congo-red, dissolved in 300 grams of water, and heated on a water-bath with 8 grams of formaldehyde solution, yields a yellow colouring matter with the same tinctorial properties as the parent substance. Bismark-brown, the indulines, &c., yield analogous products. C. H. B.

Derivatives of Orthamidobenzamide. By H. Finger (*J. pr. Chem.*, [2], **48**, 92—93; compare Abstr., 1888, 948).—*Orthamidobenzethyleneamide*, $C_2H_4(NH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2)_2$, obtained from isatoic acid and ethylenediamine, crystallises in pale, rose-coloured, lustrous laminæ, and melts at 245°. Treatment with potassium nitrite and an acid converts it into *ethylenebenzazimide*, $C_2H_4(N<\begin{matrix}N{:}N\\CO\end{matrix}>C_6H_4)_2$, which crystallises in yellowish-white, lustrous needles, and melts at 216°.

Orthamidobenzhydrazine, $NH_2{\cdot}C_6H_4{\cdot}CON_2H_3$, is prepared by adding isatoic acid to a hot solution of hydrazine sulphate and potassium hydroxide; it crystallises in monoclinic prisms and needles, and melts at 121°; it reduces Fehling's solution. With benzaldehyde, it forms a yellow, crystalline *condensation product*, melting at 158—159°. A. G. B.

Anhydrisation of Oximido-acids. By A. Hantzsch and A. Miolati (*Zeit. physikal. Chem.*, **11**, 737—750).—Oximido-acids which have the NOH group in the β- or γ-position exist as a rule only in the form of internal anhydrides—the oxazolones, which when treated with alkalis are converted more or less readily into the alkaline salts of the original acids. The authors have studied the rate at which this splitting of the oxazolone ring takes place, in order to ascertain the effect of various hydrocarbon radicles in the molecule in furthering or preventing the formation of internal anhydrides.

The anhydrides of the β-oximido-acids are so readily attacked by alkalis that the rate at which they are converted into salts cannot be measured even at extreme dilutions. The best results were obtained with the anhydrides of γ-oximido-acids derived from phthalic acid, which are of the type $C_6H_4<\begin{matrix}CR{:}N\\CO{\cdot}O\end{matrix}$. As these anhydrides are insoluble in cold water, the measurements were made in 90 per cent. alcohol. The temperature of experiment was 25°, and the dilution was 1/200 normal. The following table contains the velocity constants found:—

R.	Const.	R.	Const.
Isopropyl	0·52	Benzyl	1·07
Normal propyl	0·65	Methyl	1·12
Ethyl	0·74	Phenyl	2·59

From these numbers, it appears that the phenyl group protects the

oxazolone ring much less than the alkyl radicles, the protecting influence of which increases with their molecular weight and with the number of methyl groups contained in them. J. W.

Phenyldithiobiuret. By E. Fromm (*Annalen*, **275**, 20—49).—Phenyldithiobiuret, when quite pure, melts at 184°. The preparation of α-phenyldithiodimethylketuret, which is now stated to melt at 236°, and of its dibenzyl derivative have been already described (Abstr., 1892, 844). Dibenzylic imidodithiooxalate (*loc. cit.*) yields biuret on treatment with alcoholic ammonia.

α-Phenyldithiophenylalduret, $NPh{:}C(SH)\cdot N{<}\begin{matrix}C(SH)\\CHPh\end{matrix}{>}N$, is obtained by treating molecular proportions of α-phenyldithiobiuret and benzaldehyde with dry hydrogen chloride; it forms lustrous leaflets, melts at 227°, and yields a *dibenzyl* derivative which crystallises in white needles, and melts at 112°.

When α-phenyldithiobiuret is oxidised with alcoholic iodine, ferric chloride and hydrochloric acid, with potassium ferricyanide, ammonium chloride, and ammonia, or with hydrogen peroxide and hydrochloric acid, a weak *base*, $C_8H_7N_3S_2$, named by the author *thiuret*, is obtained; it crystallises both from water and from alcohol with solvent of crystallisation which is only eliminated by keeping it over concentrated sulphuric acid in a vacuum. The *hydriodide*, $C_8H_7N_3S_2,HI$, crystallises from methyl or ethyl alcohol with 1 mol. of the solvent, and melts at 104° and 110° respectively with decomposition. When this salt is crystallised from concentrated hydrochloric acid, the hydrochloride is obtained; it crystallises from water with $3H_2O$, and from alcohol with 1EtOH, the melting point being in the latter case 214°. The *hydrobromide* melts at 253°; the *borate* at 144°; the *salicylate* at 76°; the *orthocresotate* at 75°; and the *paraphenylsulphonate* at 215°. Thiuret is converted into α-phenyldithiobiuret on reduction with zinc and hydrochloric acid; when distilled with 10 per cent. soda, it yields α-phenyldithiobiuret, aniline, and ammonia, whilst heating in a sealed tube at 165° with contrated hydrochloric acid decomposes it into hydrogen sulphide, sulphur, carbonic anhydride, ammonia, and v. Hofmann's methenylamidophenylmercaptamine, $C_6H_4{<}\begin{matrix}S\\N\end{matrix}{>}CNH_2$ (Abstr., 1880, 884), which, according to the author, melts at 132°. The author, therefore, regards the formula $NPh\cdot C{<}\begin{matrix}S\cdot S\\NH\end{matrix}{>}C\cdot NH_2$, as the most probable for thiuret. A. R. L.

Penta-substituted Dithiobiurets. By O. Billeter (*Ber.*, **26**, 1681—1688).—*Dimethylphenylthiocarbamide*, $NMe_2\cdot CS\cdot NHPh$, prepared from dimethylamine and phenylthiocarbimide, crystallises in large, colourless needles, and melts at 132—132·5°. *Diethylphenylthiocarbamide*, $NEt_2\cdot CS\cdot NHPh$, obtained from diethylamine and phenylthiocarbimide, does not crystallise. *Dipropylphenylthiocarbamide*, $NPr^n_2\cdot CS\cdot NHPh$, prepared from dipropylamine and phenylthiocarbimide, is deposited in needles which melt at 66°. *Diamylphenylthiocarb-*

amide, $N(C_5H_{11})_2{\cdot}CS{\cdot}NHPh$, obtained from diamylamine and phenylthiocarbimide, crystallises in lustrous plates, and melts at 72—72·3°. *Dimethylethylthiocarbamide*, $NMe_2{\cdot}CS{\cdot}NHEt$, prepared from dimethylamine and ethylthiocarbimide, forms colourless needles melting at 37—37·5°. *Dipropylethylthiocarbamide*, $NPr^{\alpha}_2{\cdot}CS{\cdot}NHEt$, obtained from dipropylamine and ethylthiocarbimide, and *diethylphenylthiocarbamide*, $NEt_2{\cdot}CS{\cdot}NHPh$, prepared from diethylamine and phenylthiocarbimide, are very similar in crystalline form, and melt at 34—34·5°.

Dimethylthiocarbamine chloride, $NMe_2{\cdot}CSCl$, crystallises in yellow prisms melting at 42°. *Diethylthiocarbamine chloride*, $NEt_2{\cdot}CSCl$, is deposited in yellow prisms, melts at 46·2—46·5°, and boils at 108° under a pressure of 10 mm. *Dipropylthiocarbamine chloride*, $NPr^{\alpha}_2{\cdot}CSCl$, is a yellow liquid boiling at 124·2—124·3° under a pressure of 10 mm. *Diamylthiocarbamine chloride*, $N(C_5H_{11})_2{\cdot}CSCl$, resembles the preceding compound and boils at 155—170° under 16 mm. pressure. These compounds were prepared in the manner previously described (Abstr., 1887, 822).

Dimethylethyldiphenyldithiobiuret, $NMe_2{\cdot}CS{\cdot}NPh{\cdot}CS{\cdot}NEtPh$, is prepared by heating dimethylthiocarbamine chloride with ethylthiocarbanilide, or ethylphenylthiocarbamine chloride with dimethylphenythiocarbamide, and is deposited in pale-yellow isometric crystals melting at 98·8°. *Dimethyldipropylphenyldithiobiuret*,

$$NMe_2.CS{\cdot}NPh{\cdot}CS{\cdot}NPr^{\alpha}_2,$$

is formed either from dimethylthiocarbamine chloride and dipropylphenylthiocarbamide, or from dipropylthiocarbamine chloride and dimethylphenylthiocarbamide; it is deposited in almost colourless crystals melting at 80·5—81°. *Dimethyldiethylphenyldithiobiuret*,

$$NMe_2{\cdot}CS{\cdot}NEt{\cdot}CS{\cdot}NEtPh,$$

is prepared from dimethylthiocarbamine chloride and diethylphenylthiocarbamide, or from ethylphenylthiocarbamine chloride and dimethylphenylthiocarbamide, and crystallises in yellow needles or prisms melting at 113·5—114°.

By the action of the above-mentioned thiocarbamine chlorides on the thiocarbamides at ordinary temperatures in chloroform solution and treatment of the products with potash, two compounds are obtained isomeric with the dithiobiurets, which the author proposes to term pseudodithiobiurets; they are somewhat unstable, and, on heating, are readily converted into the corresponding dithiobiuret.

α-Ethylpropyltriphenylpseudodithiobiuret,

$$NPhPr^{\alpha}{\cdot}C(NPh){\cdot}S{\cdot}CS{\cdot}NEtPh,$$

is prepared from ethylphenylthiocarbamine chloride and propylthiocarbanilide, and crystallises in yellow rhombohedra, melting at 68·2—69°. The *hydrochloride* is deposited in quadratic crystals. *β-Ethylpropyltriphenylpseudodithiobiuret*, is formed from propylphenylthiocarbamine chloride and ethylthiocarbanilide, and is resinous; like the preceding compound, it is converted into ethylpropyltriphenyldithiobiuret (*loc. cit.*) on heating. *α-Dimethylethyldiphenylpseudodithiobiuret*, $NEtPh{\cdot}C(NPh)S{\cdot}CS{\cdot}NMe_2$, is prepared from dimethylthiocarbamine chloride and ethylthiocarbanilide and crystal-

lises in slender needles melting at 89·8°. The *hydrochloride* is deposited in yellow, orthorhombic crystals. *β-Dimethylethyldiphenylpseudodithiobiuret* crystallises in yellow prisms, and melts at 91·2°. The *hydrochloride* is crystalline. Both these bases are converted into the ordinary dithiobiuret (m. p. 98·8°; see above) by heating for a short time on the water-bath.

The formulæ given to the above compounds can only be regarded as provisional; the author does not attempt to distinguish by means of formulæ between the two modifications of the pseudo-derivatives, nor does he consider that there is evidence to show that they are stereoisomeric. J. B. T.

Benzoyl Derivatives of Benzoylacetone. By L. Claisen (*Ber.*, 26, 1879—1881).—When the sodium salt of benzoylacetone, prepared by treating benzoylacetone with sodium ethoxide, is treated with benzoic chloride, a compound, $C_{17}H_{14}O_3$, is obtained which is similar to the dibenzoylacetone obtained by Fischer and Bülow (*Ber.*, **18**, 2133). It melts at 101—102°, and is not appreciably attacked by sodium in ethereal solution. It is, however, of strongly acid character, and dissolves easily in dilute soda forming a yellow solution. With copper acetate, it gives a bright blue copper salt, and with ferric acetate, a yellowish-brown iron salt. By repeated crystallisation from alcohol, it is converted into an isomeric compound which melts at 109—112°. E. C. R.

Orthiodobenzoic acid and some of its Derivatives. By W. Wachter (*Ber.*, **26**, 1744—1745).—The author gives an improved method for the preparation of orthiodobenzoic acid from anthranilic acid. The melting point of the pure acid is 162°. The *methylic salt* boils at 167° (25 mm.), and the *ethylic salt* at 275° (760 mm.). The *chloride* forms yellow crystals, melting at 35—40°; the *amide*, *anilide*, *ortho-* and *para-toluidides*, and the *phenylhydrazide* are crystalline substances prepared from the chloride. *Orthiodobenzophenone* is a dark coloured oil, which solidifies partially after a time. Its *oxime* melts at 150°. On treatment with hydroxylamine in alkaline solution, orthiodobenzophenone is converted in the cold into phenylindoxazen. A. H.

Iodoxybenzoic and Iodosobenzoic acids. By C. Hartmann and V. Meyer (*Ber.*, **26**, 1727—1732; compare Abstr., 1892, 1460; this vol., i, 506).—Iodoxybenzoic acid, $IO_2 \cdot C_6H_4 \cdot COOH$, is formed, together with orthiodobenzoic acid, by the action of potassium permanganate on an alkaline solution of iodosobenzoic acid. The pure acid, obtained by acidifying a solution of one of the salts, forms white needles which gradually become coloured red on exposure to light, and decompose with a sharp report when heated to 233°. It is a much stronger acid than the iodoso-derivative, reddens litmus strongly, decomposes carbonates, and has an intensely acid taste. It reacts quantitatively with acid solutions of potassium iodide, iodobenzoic acid being formed and iodine liberated. The *silver salt*, with $\frac{1}{2}H_2O$, crystallises from hot water, in which it is only slightly soluble, in groups of small, yellowish plates, and explodes on heating. The

barium and *calcium* salts are amorphous, and soluble in water, whilst the *lead* and *mercuric* salts are insoluble. The acid is decomposed by boiling aqueous soda into sodium iodate and benzoate; no salicylic acid being formed. It has been found impossible to prepare ethereal salts of the acid; methyl alcohol and hydrochloric acid produce *iodosobenzoic anhydride*, $(IO\cdot C_6H_4\cdot CO)_2O$, which may also be obtained by the action of the same reagents on iodosobenzoic acid itself; it is a white, crystalline substance, which melts at 219—220°, and is insoluble in sodium carbonate solution. Ethyl alcohol and hydrochloric acid, on the other hand, yield only orthiodobenzoic acid, and the ethylic salt of this acid is formed by the action of ethylic iodide on silver iodoxybenzoate. Phosphoric chloride acts violently on the acid, causing it to deflagrate, but in solution in phosphorus oxychloride iodosobenzoic acid and its anhydride are formed. Free iodoxybenzoic acid gives characteristic colour reactions with aniline, aniline hydrochloride, and phenol, and is decomposed by boiling sulphuric acid with liberation of iodine.

Iodosobenzoic acid reacts with isobutylamine in acetic acid solution in the same way as with ethylamine, orthiodobenzoic acid being formed. A. H.

Iodoso- and Iodoxy-derivatives of Metanitropariodobenzoic acid. By L. S. Allen (*Ber.*, **26**, 1739—1744; compare foregoing abstracts).—*Para-iodosometanitrobenzoic acid* (this vol., i, 508) is a fiery yellow-coloured, amorphous powder, resembling lead chromate in appearance. It has no definite melting point, but decomposes and becomes liquid from 190° to 205°. It dissolves to a very slight extent in glacial acetic acid, but is insoluble in all other ordinary solvents. The acid is sufficiently strong to decompose carbonates, and it forms amorphous salts with barium, silver, lead, copper, and other of the heavy metals. With acid solutions of potassium iodide, it reacts in the characteristic manner, para-iodometanitrobenzoic acid being formed, and, like ortho-iodosobenzoic acid, is simply reduced by the action of alcohol and hydrochloric acid, no ethereal salt being produced. Caustic soda decomposes it into sodium metanitro- and pariodometanitro-benzoates and iodate.

Pariodoxymetanitrobenzoic acid, $IO_2\cdot C_6H_3(NO_2)\cdot COOH$, is formed by the action of potassium permanganate in acid solution on the iodoso-acid. It is a yellow powder, slightly soluble in hot alcohol and water. When slowly heated, it commences to decompose at 180°, but when rapidly heated in a melting-point tube, it explodes violently.

Metaiodo-orthobenzoic acid does not yield an iodoso-derivative when treated by the usual methods. A. H.

Metallic Compounds of the Benzene Series. By G. Perrier (*Compt. rend.*, **116**, 1298—1300).—Benzoic chloride, when boiled with aluminium chloride in presence of carbon bisulphide, yields the compound $(PhCOCl)_2Al_2Cl_6$ in large, colourless lamellæ, which readily alter when exposed to air, and yield aluminium chloride, hydrogen chloride, and benzoic acid when treated with water.

If a mixture of this compound with diphenyl is boiled with carbon bisulphide, hydrogen chloride is evolved, and, on cooling, the compound $(C_6H_5\cdot CO\cdot C_6H_4\cdot C_6H_5)_2Al_2Cl_6$ separates in large, yellow needles, identical with those obtained by heating benzoyldiphenyl with aluminium chloride in presence of carbon bisulphide. When treated with water, the compound yields aluminium chloride and parabenzoyldiphenyl.

Retene, under the same conditions, yields red crystals of the compound $(C_6H_5\cdot CO\cdot C_{18}H_{17})_2Al_2Cl_6$, and β-naphthol yields the golden-yellow compound $(C_6H_5\cdot CO\cdot C_{10}H_7)_2Al_2Cl_6$.

Phthalic chloride and butyric chloride seem to behave in a similar manner.

From these results, it would follow that in Friedel and Craft's method for the synthesis of the acetones, the acid chloride first combines with aluminium chloride, yielding the compound

$$(RCOCl)_2Al_2Cl_6,$$

which is then acted on by the hydrocarbon or the phenol. The quantity of aluminium chloride necessary increases with the stability of this intermediate compound. C. H. B.

Molecular Weight of Hydrogen Peroxide and of Benzoyl Peroxide. By W. R. Orndorff and J. White (*Amer. Chem. J.*, **15**, 347).—The authors have confirmed the result obtained by Carrara (this vol., ii, 163), that the molecular formula of hydrogen peroxide as determined by the freezing point method is H_2O_2, and not H_4O_4 as found by Tammann (Abstr., 1890, 106). The molecular weight of benzoyl peroxide calculated from the freezing point of its solutions in benzene and acetic acid, and from the boiling point of its solutions in ether and chloroform, was found to correspond with Brodie's formula, Bz_2O_2. A. H.

Phenylic Hippurate and its Condensation Products. By F. Weiss (*Ber.*, **26**, 1699—1702).—*Phenylic hippurate*,

$$NHBz\cdot CH_2\cdot COOPh,$$

is prepared by the action of phosphorus oxychloride (6—8 grams) on a mixture of hippuric acid (10 grams) and phenol (7 grams), and crystallises from alcohol in colourless plates melting at 104°. By the further action of phosphorus oxychloride on this compound, a condensation product, $C_{15}H_{11}NO_2$, is formed, crystallising from alcohol in long, colourless needles melting at 42°. The yield is 60—70 per cent. of the phenylic salt employed. The compound is volatile with steam and is not acted on by soda; it is readily hydrolysed by hydrochloric acid with the formation of phenol, hippuric acid, glycocine, and benzoic acid; its constitution is therefore probably represented by the formula $NBz<\overset{CH}{\underset{COPh}{\|}}$, but it is at present impossible to decide definitely between this and the formula

$$\overset{N\,-}{\underset{CPh}{\|}}>CH\cdot COOPh.$$

J. B. T.

Condensation of Hippuric acid with Phthalic Anhydride and with Benzaldehyde. By E. Erlenmeyer, Jun. (*Annalen*, **275**, 1—8).—When a mixture of hippuric acid and phthalic anhydride, in molecular proportion, is heated on the water-bath for half an hour with acetic anhydride (3 mols.), the *lactimide*, $C_6H_4<\begin{matrix}CO\cdot O\\ \\ \end{matrix}>C:C<\begin{matrix}N\cdot COPh\\ |\\ CO\end{matrix}$, is obtained; it crystallises from boiling nitrobenzene in canary-yellow needles, commences to darken at 240°, and decomposes at a high temperature.

Benzoylamidocinnamic lactimide, $CHPh:C<\begin{matrix}NCO\cdot Ph\\ |\\ CO\end{matrix}$, together with *sodium benzoylamidocinnamate*, is obtained in a similar manner from benzaldehyde, hippuric acid, sodium acetate, and acetic anhydride; it crystallises from benzene in long, yellowish needles, and melts at 165—166°. A. R. L.

Parachlororthotoluic acid and its Derivatives. By A. Claus and Stapelberg (*Annalen*, **274**, 285—304).—When 1 : 2-acetotoluidine is dissolved in glacial acetic acid and treated with bleaching powder solution, the *chloro*-derivative [NHAc : Me : Cl = 1 : 2 : 4] is obtained, together with a dichloro-derivative (see below). The monochloro-derivative forms colourless, silky needles, melts at 140°, and, when boiled with alcoholic potash for 8—10 hours, yields the chlorotoluidine [NH_2 : Me : Cl = 1 : 2 : 4]; this base boils at 246°, and melts at 16° (compare Abstr., 1886, 1022). The corresponding *nitrile* obtained by the diazo-reaction (cuprous cyanide in the cold) forms yellowish needles, has a faint odour, melts at 67°, is sparingly soluble in hot water, and readily volatile with steam; parachlororthotoluic acid, formed by boiling the nitrile with alkalis, melts at 172°, and not at 130°, as stated by Krüger (Abstr., 1885, 1053). The constitution of the acid is proved by the fact that it yields 1 : 2 : 4-chlorophthalic acid on oxidation. The *potassium* salt forms colourless needles with $1H_2O$; the *calcium* salt crystallises with $3H_2O$; the *barium* salt with $4H_2O$; the *amide* melts at 183°; and the *ethylic* salt at 258°.

The dichloracetotoluidine mentioned above [NHAc : Me : Cl_2 = 1 : 2 : 4 : 6] forms delicate needles or thin plates, melts at 186°, and yields the corresponding *derivative* of orthotoluidine when boiled with alcoholic potash; the latter is sparingly volatile with steam, forms colourless, lustrous needles, melts at 53°, and is converted into the *nitrile* melting at 92° by the diazo-reaction. When the nitrile is boiled with alcoholic potash, the *dichlorotoluic acid* is obtained; it crystallises in small, colourless needles, and melts at 181°.

When the nitrate of chlorotoluidine [NH_2 : Me : Cl = 1 : 2 : 4], which crystallises in bright red plates, and melts at 183° with decomposition, is added to cooled pure sulphuric acid (16—17 parts), the *nitro*-derivative [NH_2 : Me : Cl : NO_2 = 1 : 2 : 4 : 5] is obtained; it crystallises in yellow needles, and melts at 128°. When, however, the nitrate is added to 66 per cent. sulphuric acid (25 parts), and at the end of six hours the solution is poured on to ice, the last-mentioned nitro-derivative is precipitated, whilst if the mother liquor is then nearly neutralised, the *isomeride* [NH_2 : Me : Cl : NO_2 = 1 : 2 : 4 : 6] sepa-

rates; the latter crystallises in golden leaflets, and melts at 118—119°; the *acetyl* derivative is obtained by nitrating chloracetotoluidine dissolved in concentrated sulphuric acid with nitric acid (sp. gr. 1·45); it melts at 187°. *Nitrochlorotoluonitrile* [CN : Me : Cl : NO_2 = 1 : 2 : 4 : 6] melts at 140°, and yields the corresponding *nitrochlorotoluic acid* melting at 189°. *Nitrochlorotoluonitrile* [CN : Me : Cl : NO_2 = 1 : 2 : 4 : 5] melts at 86°, and the corresponding nitrochlorotoluic acid melts at 193°; the *potassium* salt crystallises with $\frac{1}{2}H_2O$, and the *magnesium* salt with $4H_2O$; the chlorine atom is displaced by the anilido-group when the acid is heated at 160—170° with aniline (compare Schöpff, Abstr., 1892, 535). The last-mentioned nitrochlorotoluic acid is the principal product of the action of nitric acid (sp. gr. 1·52) at 110—120° on parachlororthotoluic acid, but the isomeride

[COOH : Me : NO_2 : Cl = 1 : 2 : 3 : 4],

melting at 186°, is formed in smaller amount. The two acids are separated by means of their magnesium salts, that of the acid melting at 186° being the more soluble in water. The nitro-acid (m. p. 186°) is, however, obtained in good yield when parachlororthotoluic acid is heated at 100° with 10 parts of nitric acid of sp. gr. 1·52 and 30 parts of concentrated sulphuric acid; the *potassium* salt crystallises with $1H_2O$, and the *magnesium* salt crystallises with $5H_2O$.

When parachlororthotoluic acid is boiled with a mixture of nitric and sulphuric acids, or is heated with it in a sealed tube at 160°, the *dinitro*-derivative [COOH : Me : $(NO_2)_2$: Cl = 1 : 2 : 3 : 5 : 4], melting at 212°, is formed. A. R. L.

Iodoxy- and Iodoso-derivatives of Paratoluic acid. By E. Kloeppel (*Ber.*, **26**, 1733—1738; compare this vol., i, 506).—*Metaiodoparatoluic acid*, $C_6H_3MeI{\cdot}COOH$ [Me : I : COOH = 1 : 2 : 4], is obtained from the corresponding amido-acid by means of the diazo-reaction. It crystallises from ether in long, white needles, is readily soluble in alcohol, slightly in hot water, and melts at 205—206°. This acid does not yield an iodoso-derivative, either by v. Meyer's method (Abstr., 1892, 1460), or by that of Willgerodt (Abstr., 1893, i, 149). On boiling with fuming nitric acid, however, a *nitro-iodosoparatoluic acid* is formed as an amorphous powder, melting at about 160°. Metaiodoparatoluic acid, therefore, behaves in a similar manner to the meta- and para-iodobenzoic acids (this vol., i, 508).

Ortho-iodoparatoluic acid [Me : I : COOH = 1 : 3 : 4] can also be prepared by means of the diazo-reaction, and forms white needles which melt at 127°. This acid behaves in a similar manner to ortho-iodobenzoic acid (this vol., i, 507), forming a dichloride, which on treatment with aqueous soda yields *iodosoparatoluic acid*; this separates from a large quantity of water in small crystals, which soften at 120°, and melt with decomposition at 167—169°. The *silver salt* does not explode on heating. A. H.

α-Benzoylamidophenylpropionic acid. By E. Erlenmeyer, Jun. (*Annalen*, **275**, 13—20).—*α-Benzoylamidophenylpropionic acid*, $CH_2Ph{\cdot}CH(NHBz){\cdot}COOH$, is prepared by reducing benzoylamidocinnamic acid with a slight excess of 2 per cent. sodium amalgam; it forms lustrous leaflets, melts at 182—183°, and is much more

stable towards alkalis than benzoylamidocinnamic acid. When heated with concentrated hydrochloric acid in a sealed tube at 150° for 15 hours, it yields phenylalanine and benzoic acid. A. R. L.

Separation of Cinnamic acid Dibromide into its Optically Active Components. By E. Erlenmeyer, Jun. (*Ber.*, **26**, 1659—1662).—The dibromide is separated by fractional precipitation with cinchonine, and by crystallisation of the cinchonine salts from alcohol. The dextrorotatory acid has been obtained with the rotation $[\alpha]_D = +48{\cdot}15°$. E. C. R.

Optically Active Cinnamic acid Dibromides. By C. Liebermann (*Ber.*, **26**, 1662—1663).—A question of priority.

Optically Active Cinnamic acid Dibromides. By C. Liebermann and A. Hartmann (*Ber.*, **26**, 1664—1666).—The authors give an account of their attempt to quantitatively separate the optically active constituents. They have been only partially successful; but have proved that cinnamic acid dibromide contains only two optically active constituents.

The ethylic salt of dextro-rotatory cinnamic acid dibromide separates from carbon bisulphide in colourless crystals, melts at 71°, and has the rotation $[\alpha]_D = +59{\cdot}1°$. E. C. R.

Benzoylamidocinnamic acid. By E. Erlenmeyer, Jun. (*Annalen*, **275**, 8—13).—*Benzoylamidocinnamic* acid,

$$CHPh{:}C(NHBz){\cdot}COOH,$$

is obtained when the lactimide (last abstract) is suspended in water and heated with a slight excess of dilute sodium hydroxide, or with dilute sulphuric acid; the former reagent acts the more readily. It crystallises from alcohol in transparent prisms, and melts (according to its purity) between 210° and 228°, yielding the lactimide, phenylacetaldehyde, and carbonic anhydride; by energetic treatment with mineral acids or alkalis, it is decomposed with the formation of benzamide and phenylpyruvic acid, and on oxidation with potassium permanganate in alkaline solution it yields benzaldehyde. The *ethylic* salt is obtained by treating the lactimide with sulphuric acid and alcohol, or by adding sodium and a little alcohol to a mixture of ethylic hippurate and benzaldehyde suspended in ether; it forms delicate needles, and melts at 149°. A. R. L.

Abietic acid. By H. Mach (*Monatsh.*, **14**, 186—201).—The various substances hitherto obtained from the resin of pine trees, and named respectively abietic, sylvic, and pimaric acids, are shown to be identical; the name *abietic acid* is retained. This acid occurs in colophonium in varying amount; some specimens of the resin contain 90 per cent. of the crude acid, from others no acid could be isolated. The method usually adopted was to digest the resin with 70 per cent. alcohol, and recrystallise the residual acid from methyl alcohol; or, in some cases, the crude acid was dissolved in 90 per cent. alcohol, precipitated with hydrochloric acid, and recrystallised from methyl

alcohol. Analyses and molecular weight determinations (cryoscopic and ebullioscopic) agree with the formula $C_{19}H_{28}O_2$. The acid forms white crystals, and melts at 153—154° when slowly heated, beginning to soften at 148°. The *potassium salt*, $C_{19}H_{27}KO_2,3C_{19}H_{28}O_2$, was prepared by neutralising an alcoholic solution of the acid with alcoholic potash, or boiling it with potassium carbonate; it forms bundles of silky needles, and melts at 183°. C. F. B.

Formation of Inner Anhydrides from Ketoximic acids. By A. Hantzsch and A. Miolati (*Ber.*, **26**, 1689—1691).—*Ethylbenzoylacetic acid oxime*, NOH:CPh·CHEt·COOH, is prepared by the action of hydroxylamine on the ethereal salt in alkaline solution, and forms colourless crystals melting at 89—90°. It is not acted on by acetic anhydride or concentrated sulphuric acid.

Ethylic hydrogen acetylmalonate oxime,

NOH:CMe·CH(COOEt)·COOH,

is obtained from ethylic acetylmalonate and crystallises from dilute alcohol in small, colourless needles melting at 148°. The compound does not appear to form an anhydride, nor could it be hydrolysed; attempts to eliminate a carboxyl group were also unsuccessful. The authors point out the importance of both the position and nature of radicles in determining the formation of anhydrides from oximes; thus in the case of β-ethoximic acids, whilst hydrocarbon radicles directly linked to the C:NOH group facilitate the formation of anhydrides, their action is precisely the reverse when they are linked to a carbon atom which is itself linked to carboxyl, as in the group

–C(NOH)·CHR·COOH;

the same applies when R = COOH. This probably explains the failure of dimethylglyoxime, which is a "syn-" compound, to form an aldehyde. J. B. T.

Addition of Sodium Alkyloxides. By C. Liebermann (*Ber.*, **26**, 1876—1879).—The author has obtained direct additive compounds of sodium ethoxide and ethylic malonates of the general formula $>C:C(COOH)_2$.

Ethylic ethoxybenzylsodiomalonate, OEt·CHPh·CNa(COOEt)$_2$, is obtained by adding sodium ethoxide to an ethereal solution of ethylic benzalmalonate. It is a white powder which is decomposed by water into alkali and ethylic ethoxybenzylmalonate,

OEt·CHPh·CH(COOEt)$_2$.

Methylic methoxybenzylsodiomalonate, ethylic ethoxyfurfurylsodiomalonate, ethylic ethoxypiperonylsodiomalonate, and methylic methoxypiperonylsodiomalonate have also been prepared.

These sodium compounds are only alkylated with difficulty, and on heating for a day with ethylic iodide at 100° the reaction had only partially taken place. E. C. R.

Bromogallic acid and its Derivatives. By A. Bétrix (*Bull. Soc. Chim.* [3], **9**, 241—243).—Bromogallic acid is difficult to separate from the dibromo-acid which is formed at the same time by the ordinary

method of preparation. The former is obtained together with unaltered gallic acid, from which it is readily separated by crystallisation, when less than the theoretical quantity of bromine dissolved in chloroform (3—4 parts) is gradually added to gallic acid. The pure acid, $C_6HBr(OH)_3{\cdot}COOH + 3H_2O$, crystallises in small, hexagonal tables; the *acetyl* derivative melts at 95—96°. When barium hydroxide is added to a solution of the *ammonium* salt, a yellowish-orange coloration changing to green is produced; and on the addition of lead acetate to a solution of the ammonium salt, the *lead* salt separates as a white precipitate which later becomes green and finally dirty grey; the salt decomposes on fusion. A. R. L.

Alkyltoluidinesulphonic acids. By R. Schmidt (*J. pr. Chem.* [2], **48**, 46—69; compare Abstr., 1887, 1043—1044; 1891, 908; 1892, 334).—When potassium paratoluidinemetasulphonate is heated in a sealed tube with the calculated quantity of ethylic bromide and absolute alcohol at 150°, potassium sulphate and an oil are produced. The latter partially crystallises, and the portion which remains liquid is a mixture of ethyltoluidine and diethyltoluidine.

Diethyltoluidine hydrochloride melts at 157° and dissolves in alcohol, water, and warm benzene. Ethyltoluidine hydrochloride appears to be very unstable.

The crystalline *compound* forms colourless, monoclinic prisms (with $1H_2O$), melts at 243°, and is soluble in water and sparingly in absolute alcohol, but not in ether and benzene. Its molecular formula corresponds with that of diethyltoluidinesulphonic acid, but the *potassium salt*, $C_{11}H_{14}NSO_3K$, is the only salt which could be prepared; this crystallises in rhomboidal tables, melts at 297°, and dissolves in water.

Diethylparatoluidineorthosulphonic acid, $NEt_2{\cdot}C_6H_3Me{\cdot}SO_3H + H_2O$, is obtained both by sulphonating diethyltoluidine and by heating potassium paratoluidineorthosulphonate with ethylic bromide in absolute alcohol; in the latter case, potassium sulphate is not a product of the reaction (compare above). The acid crystallises in beautiful, colourless prisms which are infusible, and are only sparingly soluble in water and in alcohol. The *potassium* salt crystallises in colourless, triclinic tables with $2H_2O$. The barium salt, with $4H_2O$, and the *calcium* salt, with $3H_2O$, were also crystallised.

The author discusses the possible constitution of the substance which melts at 243°, but does not arrive at any definite conclusion.

Ethylparatoluidineorthosulphonic acid, $NHEt{\cdot}C_6H_3Me{\cdot}SO_3H + H_2O$, is prepared by sulphonating ethyltoluidine; it crystallises in yellow prisms and is sparingly soluble in water and alcohol. The *potassium* salt crystallises in yellow tables with $1H_2O$, and is freely soluble in water. When the potassium salt is heated with ethylic bromide, it yields diethylparatoluidineorthosulphonic acid; the potassium salt of the latter acid remains unchanged when similarly treated.

By heating potassium paratoluidinemetasulphonate with isopropylic bromide, a *compound*, $C_{13}H_{21}NSO_3$, apparently containing two isopropyl groups, is obtained. It crystallises from water, and melts at 222—223°. When potassium paratoluidineorthosulphonate is similarly treated, an *isopropyltoluidinesulphonic acid* is obtained; it dis-

solves sparingly in water and very sparingly in alcohol, and crystallises in colourless prisms which do not melt at 300°.

A. G. B.

Action of some Alcohols on Paradiazotoluenemetasulphonic acid. By W. V. METCALF (*Amer. Chem. J.*, **15**, 301; compare Abstr., 1887, 136; 1888, 268; 1889, 975; this vol., i, 325).—This substance, like the corresponding orthodiazo-compound, when boiled with alcohol under a *plus* pressure of 200 mm., yields a considerable proportion of ethoxytoluenesulphonic acid in addition to metatoluenesulphonic acid. The corresponding sulphonamides are difficult to separate, the mixture having been mistaken by v. Pechmann (*Annalen*, **169**, 47) for the pure metatoluenesulphonic acid.

Parethoxytoluenemetasulphonamide, $OEt\cdot C_6H_3Me\cdot SO_2NH_2$, forms white needles, slightly soluble in cold water; it melts at 138—139°. On oxidation with potassium permanganate, it yields *parethoxymetasulphonaminebenzoic acid*, which crystallises in long, white needles; it softens at 225° and melts at 230—231° with slight decomposition. The *barium salt* contains $2H_2O$. Methyl and propyl alcohol act in a similar manner to ethyl alcohol. Comparative experiments with methyl alcohol under *plus* pressures of 200, 400, and 600 mm. show that the proportion of methoxy-compound formed increases slightly with the pressure.

Paramethoxytoluenemetasulphonic chloride, $OMe\cdot C_6H_3Me\cdot SO_2Cl$, crystallises from benzene in large, rhombic plates melting at 84°. The free *acid* forms yellowish needles melting at 92—95°, and yields crystalline barium, calcium, and lead salts. The *sulphonamide* crystallises in white needles, melts at 180—181°, and is only slightly soluble in boiling water. On oxidation, it yields *paramethoxymetasulphonaminebenzoic acid*, which forms white needles, and melts with decomposition between 240° and 270°; its *barium salt* contains $3H_2O$.

Parapropoxytoluenemetasulphonamide crystallises in needles, melts at 126·5—128°, and is nearly insoluble in cold water. A. H.

Action of Methyl Alcohol on Paradiazotolueneorthosulphonic acid. By R. M. PARKS (*Amer. Chem. J.*, **15**, 320; compare preceding abstract).—This compound, when heated with methyl alcohol, yields paramethoxytolueneorthosulphonic acid alone, the course of the reaction not being influenced by increase or diminution of the pressure. The product is identical with the oxymethyltoluenesulphonic acid of Limpricht and Heffter (*Annalen*, **221**, 344). The free acid is a dark brown liquid, which crystallises with great difficulty in rhombohedral plates; these decompose on heating without melting. The *barium salt* crystallises with $3H_2O$ and the *calcium salt* with $4H_2O$. The corresponding *sulphonic chloride* is a heavy, yellowish oil; the *sulphonamide* crystallises in white plates or prisms, is very soluble in alcohol, slightly so in water, and melts at 151°. On oxidation with potassium permanganate, the sulphonamide is partially converted into *paramethoxybenzoic sulphinide*, $OMe\cdot C_6H_3<\begin{matrix}SO_2\\CO\end{matrix}>NH$, which forms long, slender needles, melts at 271°, and is easily soluble in boiling alcohol. The acid potassium salt of *paramethoxyorthosulphobenzoic*

acid is also formed in this reaction, and by the oxidation of potassium paramethoxytolueneorthosulphonate; it crystallises in long prisms containing $1H_2O$. The *chloride of the sulphobenzoic acid*, $OMe{\cdot}C_6H_3(SO_2Cl){\cdot}COCl$, forms small, colourless crystals, and on boiling with water yields the *free acid*; this substance dissolves readily in water, crystallises in long needles, and melts without decomposition at 104°. This acid yields resorcinol and 1 : 2 : 4-dihydroxybenzoic acid on fusion with potash, so that its constitution is

$$[COOH : SO_3H : OMe = 1 : 2 : 4].$$

The isomeric acid obtained by Zervas (*Annalen*, **103**, 338) by the direct sulphonation of anisic acid is therefore the 1 : 3 : 4-compound.

A. H.

Monochloro-derivatives of Ortho-xylene, and their Relation to the Chlororthotoluic acids. By A. Claus and R. Bayer (*Annalen*, **274**, 304—311).—It having been shown that the melting point of parachlororthotoluic acid is incorrectly given by Krüger (Abstr., 1885, 1053), the authors have repeated the whole of this chemist's experiments.

A mixture of about 2 parts of 4-chlorortho-xylene and 1 part of 3-chlorortho-xylene is obtained by chlorinating orthoxylene in presence of iron.

4-Chlorortho-xylene-5-sulphonic acid forms colourless needles or nacreous plates containing $5H_2O$; *3-chlorortho-xylene-6-sulphonic acid* is more sparingly soluble in water than the isomeride, and crystallises in small, prismatic needles with $2H_2O$. The two chlorortho-xylenes, obtained by the hydrolysis of the sulphonic acids, agree with Krüger's description; they were oxidised by heating with nitric acid at 160°, and the chlororthotoluic acids converted into their calcium salts. The more sparingly soluble calcium salt, with $2H_2O$, is, in accordance with Krüger's statement, derived from the acid [COOH : Me : Cl = 1 : 2 : 5], but this acid melts at 137° (not 166°); the calcium salt of the acid [COOH : Me : Cl = 1 : 2 : 4] crystallises with $3H_2O$, and the acid melts at 170° (not 130°).

The acid melting at 156° [COOH : Me : Cl = 1 : 2 : 3] is obtained by oxidising 1 : 2 : 3-chlorortho-xylene, as stated by Krüger. The two meta-acids, melting at 137° and 156° respectively, are obtained (the former predominating) by passing chlorine into a solution of orthotoluic acid in glacial acetic acid.

A. R. L.

α-Hydrindone and its Derivatives. By A. König (*Annalen*, **275**, 341—351; compare Gabriel and Hausmann (Abstr., 1889, 1172). —Hydrocinnamorthocarboxylic acid was prepared, as already described (Abstr., 1888, 150). When either the acid or its calcium salt, preferably the former, is distilled, α-hydrindone is formed; it melts at 40—41°, boils at 241—242° (739 mm.), has a sp. gr. at 42° = 1·099, and yields phthalic acid on oxidation with nitric acid. The oxime melts at 144—144·5°, and the hydrazone melts at 130—131°. When α-hydrindone is dissolved in glacial acetic acid (10 parts), and chlorine passed through the boiling solution, a *dichloro*-derivative, $C_9H_6Cl_2O$, is obtained, which crystallises in thick needles,

and melts at 74—74·5°; whilst when a boiling solution of α-hydrindone in an equal weight of glacial acetic acid is treated with chlorine, tetrachlorhydrindone (Zincke and Frölich, Abstr., 1887, 955) is formed; it melts at 104·5—105·5°.

α-Amidohydrindene, $\begin{matrix}CH_2\cdot CH_2\\ C_6H_4 \text{ —}\end{matrix}\!>CH\cdot NH_2$, is obtained when α-hydrindoneoxime is reduced in alcoholic solution with sodium amalgam, keeping the liquid faintly acid with acetic acid meanwhile; it is a colourless oil having a faint, aniline-like odour, and boils at 220·5° under a pressure of 747 mm. The *hydrochloride* crystallises in colourless needles, and melts at 208°, and the *sulphate* forms plates, and melts at 256—257°.

α-Hydroxyhydrindene, $\begin{matrix}CH_2\cdot CH_2\\ C_6H_4 \text{ —}\end{matrix}\!>CH\cdot OH$, is not formed by reducing α-hydrindone with sodium amalgam, but it is produced when an aqueous solution of α-amidohydrindene hydrochloride is heated on the water-bath with sodium nitrite; it forms small crystals having the odour of naphthalene, and melts at 54—54·5°. It boils at 220° with partial decomposition into a hydrocarbon, which can also be obtained by heating the hydroxy-compound with zinc chloride; analysis of the hydrocarbon gave values agreeing better with those required for hydrindene than for indene. A. R. L.

β-Hydrindone and its Derivatives. By H. Benedikt (*Annalen*, **275**, 351—356).—*β-Hydrindone*, $C_6H_4\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>CO$, is obtained by distilling dehydrated calcium orthophenylenediacetate; it crystallises in colourless, flat needles, has the odour of jasmine, melts at 61°, is volatile with steam, boils with partial decomposition at 220—225°, and is converted into a brown, viscid mass on exposure to the air. Wislicenus has already published a preliminary account of this compound (*Tageblatte d. Naturforsch.-Versamm.*, 1889), and he, therefore, claims the priority of its discovery over Schad (this vol., i, 280).

When β-hydrindone is oxidised with warm nitric acid, it yields phthalic acid, but is converted into homophthalic acid (W. Wislicenus, Abstr., 1886, 879) when an ethereal solution is shaken with an aqueous solution of potassium permanganate. The *oxime*, $C_6H_4\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>C\!:\!NOH$, melts at 155°, and when treated with sodium amalgam in glacial acetic acid solution, yields a small quantity of the amido-base. A. R. L.

Synthesis of α-Phenylindoxazen from Orthamidobenzophenoneoxime. By F. v. Meyenburg (*Ber.*, **26**, 1657—1658).—Phenylindoxazen, $C_6H_4\!<\!\begin{matrix}CPh\\ O \text{ —}\end{matrix}\!>N$, is obtained by adding sodium nitrite to a solution of orthamidobenzophenoneoxime in excess of very dilute hydrochloric acid, and after quickly filtering the mixture, heating it over a bare flame. It crystallises well, and melts at 83—84°. Only the pure high melting modification of orthamidobenzophenoneoxime is convertible into phenylindoxazone. E. C. R.

Orthodiamidodiphenyl. By E. Täuber (*Ber.*, **26**, 1703—1705; compare Abstr., 1891, 570).—Carbazole is obtained by heating orthotetrazodiphenyl with potassium hydrosulphide on the water-bath in aqueous solution, but the author is at present unable to explain its formation.

It has been previously shown (this vol., i, 96) that orthodiamidodiphenyl combines with benzile, and that the compound which is formed yields a reduction product $\begin{matrix}C_6H_4\cdot NH\cdot CHPh\\ |\\ C_6H_4\cdot NH\cdot CHPh\end{matrix}$; the dinitroso-derivative has now been analysed. The *diacetyl derivative* is deposited from acetic acid in granular crystals melting at 280°. The above reduction compound is not acted on by heating with 20 per cent. hydrochloric acid.

Diamidoditolyl, $NH_2\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2$ [$C_6H_3 : NH_2 : Me = 1 : 2 : 5$], reacts with benzile in a similar manner to diamidodiphenyl; the yellow condensation product melts at 235°, and on reduction yields a colourless, basic compound melting at 163°. J. B. T.

Tetramethoxydiphthalyl. By R. Löwy (*Monatsh.*, **14**, 131—145).—Tetramethoxydiphthalyl (compare Goldschmidt and Egger, Abstr., 1891, 1371), when warmed with alcoholic potash in an atmosphere of hydrogen, is converted into *tetramethoxydiphthalyllactonic acid*, $COOH\cdot C_6H_2(OMe)_2\cdot C(OH):C<\begin{matrix}C_6H_2(OMe)_2\\ O\end{matrix}>CO$, and a little tetramethoxydiphthalyldicarboxylic acid. The former acid was obtained in yellow crystals, which melt with decomposition at 284—292°; the *copper salt*, $C_{40}H_{34}O_{18}Cu$, as a greenish-blue precipitate. When tetramethoxydiphthalyl is reduced with zinc and potash, it yields *tetramethoxyhydrodiphthalyllactonic acid*,

$$COOH\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH<\begin{matrix}C_6H_2(OMe)_2\\ O\end{matrix}>CO,$$

which forms white crystals, melting at 186—187°. When boiled with hydriodic acid and phosphorus, tetramethoxydiphthalyl yields *tetrahydroxydibenzyldicarboxylic acid*, $C_2H_4[C_6H_2(OH)_2\cdot COOH]_2$, as a yellow, crystalline substance, which turns greenish by oxidation on exposure to air, and melts above 300°; the *barium salt*, $C_{16}H_{12}O_8Ba + H_2O$, forms greenish-yellow crystals. Tetramethoxydiphthalyl takes up two atoms of bromine when boiled with the latter in chloroform solution, yielding *tetramethoxydiphthalyl dibromide*, which crystallises in lemon-yellow, silky needles, and begins to decompose at 100°.

Tetramethoxydiphthalylimide,

$$CO<\begin{matrix}C_6H_2(OMe)_2\\ O\end{matrix}>C:C<\begin{matrix}C_6H_2(OMe)_2\\ O\end{matrix}>C:NH,$$

is obtained when tetramethoxydiphthalyllactonic acid is heated in a sealed tube with strong ammonia at 100°; it is a yellow substance, which turns brown at about 200°, but is not melted at 310°. The substances described in this paper all exhibit colour reactions with sulphuric acid, &c. In general, the behaviour and derivatives of tetramethoxydiphthalyl are analogous to those of diphthalyl itself.

C. F. B.

Preparation of Triphenylacetonitrile and Triphenylcarbinol. By L. Bouveault (*Bull. Soc. Chim.* [3], **9**, 373—375).—Triphenylcarbinol is most easily prepared by decomposing triphenylbromomethane with a solution of sodium carbonate, which, by neutralising the hydrobromic acid as fast as it is formed, greatly accelerates the action of the water (compare Hémilian, this Journal, 1875, 152).

Triphenylacetonitrile is best prepared by treating triphenylbromomethane with mercuric cyanide in the same manner as that adopted by E. and O. Fischer for the treatment of triphenylchloromethane (Abstr., 1879, 326). The product of the reaction is extracted with boiling benzene, and the solution is filtered and distilled; the residue, consisting of the nitrile, is recrystallised from ether. A. G. B.

Action of Hydroxylamine on Orthobenzoylbenzoic acid. By F. H. Thorp (*Ber.*, **26**, 1795—1796; compare this vol., i, 466).—The compound recently described by the author as the oxime of benzoylbenzoic acid is in reality its *anhydride*, which has already been prepared by Hantzsch and Miolati (this vol., ii, 574); the salts of the corresponding acid are readily obtained by dissolving the anhydride in alkali, and adding metallic salts; the *silver ammonium* salt, $NOAg{:}CPh{\cdot}COONH_4$, is a white precipitate, which becomes crystalline after a time, and darkens in the light. The *barium* salt, $C_{14}H_9O_3NBa$, is also a crystalline precipitate, and the *potassium* salt, $C_{14}H_9O_3NK_2 + 3H_2O$, forms thin, transparent plates, which are very soluble in water. H. G. C.

Condensation of Deoxybenzoïn with Aldehydes and Ketones. By F. Klingemann (*Annalen*, **275**, 50—83).—*Benzamarone* melts at 217—218°, and determinations of its molecular weight by the cryoscopic method show that it has not the formula $C_{70}H_{56}O_4$, assigned to it by Zinin, but the formula $C_{35}H_{28}O_2$; it is, therefore, formed from benzaldehyde (1 mol.) and deoxybenzoïn (2 mols.), with the elimination of 1 mol. H_2O (compare Abstr., 1889, 265).

Metanitrobenzamarone, $NO_2{\cdot}C_{35}H_{27}O_2$, is formed in a similar manner from metanitrobenzaldehyde and deoxybenzoïn; it crystallises in delicate, yellowish needles, and melts at 220°. Ethyldeoxybenzoïn does not yield a condensation derivative with benzaldehyde; hence the CH_2 group in deoxybenzoïn takes part in the reaction.

The two isomerides, $C_{21}H_{16}O$, obtained by distilling benzamarone (this vol., i, 353), crystallise in the monoclinic system; the crystals of the modification melting at 101—102° have axial relations $a : b : c = 3{\cdot}2899 : 1 : 2{\cdot}3846$; $\beta = 87°\ 8'$; whilst the crystals of that melting at 89—90° have axial relations

$$a : b : c = 0{\cdot}8389 : 1 : 1{\cdot}5537;\ \beta = 56°\ 26'.$$

Both the isomerides are converted into sodium amarate when boiled with sodium ethoxide, but no such reaction occurs when sodium methoxide is used; indeed Zinin's observation that a lower homologue of amaric acid is formed when benzamarone is heated with sodium methoxide appears to be erroneous. In the preparation of

amaric anhydride from benzamarone, it is preferable to employ sodium ethoxide instead of a solution of sodium hydroxide in alcohol, as recommended by Zinin.

Dimethylamaric acid, $C_{25}H_{26}O_3$, is obtained by cohobating benzamarone with sodium isobutoxide; it forms monoclinic crystals, $a : b : c = 2{\cdot}9249 : 1 : 2{\cdot}5452$; $\beta = 82° 57' 10''$, and melts at 182°.

When amaric anhydride is heated at 100° with alcoholic ammonia, and the product is precipitated from water, a mixture of *amaric amide*, $C_{23}H_{33}NO_2$, which crystallises in white needles, and melts at 145—152°, and an *amide*, $C_{23}H_{25}NO_3$, which forms small, flat crystals, and melts at 124°, is obtained; whilst on adding hydrochloric acid to the filtrate, the monobasic acid, $C_{23}H_{34}O_4$, from which the second amide is derived, separates; it forms small transparent prisms, melts at 127—135°, and yields amaric anhydride when heated; the *silver* salt is a flocculent precipitate fairly stable towards light.

When amaric anhydride is dissolved in glacial acetic acid, and nitric acid added, or when it is treated with alcoholic sulphuric acid, a *compound*, $C_{21}H_{18}O_2$, melting at 163—168°, is formed; on hydrolysis with alcoholic potash, it yields a soluble salt.

When amaric acid is oxidised with chromic acid or alkaline potassium permanganate, *α-* and *β-dehydroamaric* acid, $C_{23}H_{30}O_3$, are formed. The *α-acid* melts at 173°, resolidifies at a higher temperature, and then melts at 238°, which is the melting point of the *β*-acid, into which it is converted. The *anhydride*, $C_{23}H_{28}O_2$, is obtained by distilling the *β*-acid under diminished pressure; it melts at 129—130°, and when heated with alcoholic ammonia at 100°, yields a very stable amide, $C_{23}H_{31}NO_2$, melting at 232°. The *β*-acid is regenerated when the amide is treated with alcoholic potash. When *β*-dehydroamaric acid is fused with potash, it yields benzoic acid and pyroamaric acid, $C_{16}H_{16}O_2$, melting at 95—96°.

The compound $C_{36}H_{28}O_2$, melting at 198°, is obtained by the condensation of deoxybenzoïn with acetophenone, and the *compound* $C_{33}H_{28}O_3$ is obtained by the condensation of deoxybenzoïn with furfuraldehyde. A. R. L.

Diphenylacetic Acid. By F. Klingemann (*Annalen*, **275**, 83—89).—*Diphenylacetanilide*, $C_{20}H_{17}NO$, is prepared by treating an ethereal solution of diphenylacetic chloride with aniline; it forms colourless needles, and melts at 180°; the *hydrazide*, $C_{20}H_{18}N_2O$, melts at 168°; the *amide* is obtained by passing dry ammonia into an ethereal solution of the chloride; it is converted into the *nitrile* by means of phosphorus pentachloride. On ethylation, this *nitrile* yields *ethyldiphenylacetonitrile*, boiling at 183° (13 mm.); it is scarcely attacked when boiled with alcoholic potash, but on being heated in a sealed tube at 210° with a mixture of glacial acetic and hydrochloric acids it yields *ethyldiphenylacetic acid*, which forms transparent crystals, and melts at 173—174°. It is, therefore, not identical with pyroamaric acid (last abstract).

When diphenylacetic chloride is treated with benzene and aluminium, triphenylmethane is obtained together with small quantities of phenyldeoxybenzoïn, which crystallises in small, white

needles, and melts at 125—128°, and a *hydrocarbon*, $C_{28}H_{20}$, forming yellow crystals and melting at 168°. A. R. L.

Dihydronaphthalene and some of its Derivatives. By E. Bamberger and W. Lodter (*Ber.*, **26**, 1833—1844; compare Abstr., 1891, 1072).—The additional hydrogen atoms in dihydronaphthalene occupy the para- or 1 : 4-position, and not the ortho- or 1 : 2-position as was formerly supposed. This is proved by the fact that, on oxidation, it yields orthophenylenediacetic acid, $C_6H_4(CH_2{\cdot}COOH)_2$. The hydrocarbon is closely analogous to ethylene, and, like the latter, forms a *dibromide*, which is reconverted by the action of alcohol and zinc-dust into dihydronaphthalene, and, on treatment with potassium carbonate, yields *tetrahydronaphthalene glycol*, $C_{10}H_{10}(OH)_2$; this crystallises in silver-white plates, resembling naphthalene in appearance, melts at 135°, and is not volatile with steam. It dissolves to a moderate extent in cold water, and readily in hot water, alcohol, and chloroform. It has all the properties of a glycol, being insoluble in alkalis, and unacted on by diazo-compounds. The *benzoate* melts at 89—90°, the *acetate* at 109·5—110°, and the *bisphenylurethane* at 148—150° : all these derivatives being crystalline. On oxidation, it yields orthophenylenediacetic acid, together with a smaller amount of orthocarboxyphenylacetic acid, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}COOH$, and other products. On treatment with hydrogen chloride, it is converted into tetrahydronaphthalene chlorhydrin, $C_{10}H_{10}Cl{\cdot}OH$, which forms long, silky needles melting at 117·5° ; this sublimes readily at 100°, and is slightly soluble in cold water, readily in alcohol, &c. The chlorhydrin is best prepared by treating dihydronaphthalene itself with hypochlorous acid. The *acetate* forms radiating groups of prisms which melt at 47°, and deliquesce in ether or chloroform vapour; the *benzoate* crystallises in needles melting at 64—65°.

The action of alkalis on the chlorhydrin is of a complicated nature, the products of the reaction varying with the conditions of the experiment. The most readily formed of these products is *tetrahydronaphthylene oxide*, $C_6H_4<\begin{matrix}CH_2{\cdot}CH\\ |\\ CH_2{\cdot}CH\end{matrix}>O$, which is very similar in chemical properties to ethylene oxide, of which it is the closed chain analogue. This substance is dimorphous, crystallising in thick plates, which belong either to the monosymmetric or asymmetric system, according to the circumstances of crystallisation. It melts at 43·5°, volatilises with extreme readiness with steam, and distils without decomposition at 257—259° under a pressure of 715 mm. It is tolerably soluble in hot water, readily in organic solvents. Like ethylene oxide, it does not react with hydroxylamine or phenylhydrazine. It readily unites with hydrogen chloride and hydrogen bromide to form the corresponding hydrins, and even precipitates ferric hydrate from solutions of ferric chloride. It also combines, although less readily, with water, producing the glycol, and very readily with organic bases to form alkines, which closely resemble the hydroxylamines of Wurtz. Of these, the following have been prepared by the direct action of the base on the chlorhydrin :—

Dimethyltetrahydronaphthylalkine, $NMe_2 \cdot C_{10}H_{10} \cdot OH$, an alkaline oil which boils at 183° (27 mm.).

Diethyltetrahydronaphthylalkine, $NEt_2 \cdot C_{10}H_{10} \cdot OH$, boiling at 202° (38 mm.).

Piperidyltetrahydronaphthylalkine, $C_5NH_{10} \cdot C_{10}H_{10} \cdot OH$, crystallises in colourless needles melting at 46—48°.

Trimethylhydroxytetrahydronaphthylammonium hydroxide,

$$OH \cdot NMe_3 \cdot C_{10}H_{10} \cdot OH :$$

a syrup which crystallises with difficulty, and acts as an alkali. The *chloride* forms lustrous, monosymmetric prisms melting at 243°. This compound is the closed chain analogue of choline, which it resembles in all its properties.

Dihydroxytetrahydronaphthylethylenediamine, $C_2H_4(NH \cdot C_{10}H_{10} \cdot OH)_2$, forms groups of white needles, melts at 201°, and is soluble in alcohol, benzene, &c., scarcely soluble in water. Diacid base.

Hydroxytetrahydronaphthylamine, $NH_2 \cdot C_{10}H_{10} \cdot OH$, which is an alkaline oil; the *hydrochloride* forms needles melting at 265°; the *phthalimide* compound is a colourless, crystalline powder melting at 217—218·5°.

Dihydroxytetrahydronaphthylamine, $NH(C_{10}H_{10} \cdot OH)_2$, forms long, refractive prisms, melts at 165—166°, and is almost insoluble in water, but soluble in alcohol, &c.

A series of *alkeïnes* has also been prepared, but are not described in detail.

When the chlorhydrin is submitted to the continued action of an alkali, the tetrahydronaphthylene glycol becomes converted into the isomeric *dihydronaphthol*, which probably has the formula

$$C_6H_4 \begin{cases} CH_2 \cdot CH \cdot OH \\ CH : CH \end{cases}.$$

This substance is an unsaturated alicyclic alcohol, is insoluble in alkalis, &c., and readily combines with bromine. It is obtained as an oil boiling at 162—168° (28 mm.), but has probably not yet been prepared quite pure. Mineral acids at once convert it into naphthalene, and its presence can readily be recognised. The reaction with bromine is not of the nature of a simple addition, the only product which has been isolated having the composition of a brominated tetrahydronaphthyleneglycol, $C_{10}H_9Br(OH)_2$.

Dihydronaphthol is also capable, when acted on by an alcohol, of uniting with the elements of water to form *tetrahydronaphthylenemetaglycol*, $C_6H_4 \begin{cases} CH_2 \text{——} CH \cdot OH \\ CH(OH) \cdot CH_2 \end{cases}$. This compound is obtained as an oil boiling at 175—178° (20 mm.), but solidifies, on standing, to white needles melting at 49°, and can be recrystallised from light petroleum. It is insoluble in alkalis, and is not decomposed by mineral acids.

On oxidation with potassium permanganate, dihydronaphthol is converted into *dihydroisocoumarincarboxylic acid*,

$$C_6H_4 \begin{cases} CH_2 \cdot CH \cdot COOH \\ CO \cdot O \end{cases}.$$

a substance which is also formed by the action of sodium amalgam on isocoumarincarboxylic acid. This forms fascicular groups of lustrous needles, melts at 153·5°, and is readily soluble in hot water, alcohol, and boiling chloroform. It is a lactonic acid, and neutralises one equivalent of an alkali in the cold, two on heating. It is reduced by phosphorus and hydriodic acid to orthocarboxyhydrocinnamic acid. Tetrahydronaphthylene chlorhydrin is converted by the action of dilute alkalis into *monoketotetrahydronaphthalene*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CO\end{matrix}$. This substance has a pleasant ketone-like odour, and combines with sodium hydrogen sulphite and phenylhydrazine to form crystalline products. Finally, hot concentrated alkaline solutions convert the chlorhydrin into naphthalene.

A more detailed account of these researches is to be published later on in the *Annalen*. A. H.

Oxidation of Naphthalic acid. By C. Graebe and F. Bossel (*Ber.*, **26**, 1797—1799).—When naphthalic acid is oxidised by alkaline potassium permanganate, it is converted into *dicarboxyphenylglyoxylic acid*, $COOH\cdot CO\cdot C_6H_3(COOH)_2$, $[(COOH)_2 : CO = 1 : 3 : 2]$, which is a crystalline compound melting at 238° (corr.) with decomposition. During the oxidation, a portion of the acid loses carbonic anhydride, forming the carboxyorthophenylglyoxylic acid already prepared by Zincke and Breuer. The dicarboxy-acid combines with phenylhydrazine to form a *hydrazone*, and, on reduction with phosphorus and hydriodic acid, yields 1 : 2 : 6-*toluenedicarboxylic acid*, $C_6H_3Me(COOH)_2$, which melts without decomposition at 235°, and is oxidised by alkaline permanganate to hemimellitic acid, $C_6H_3(COOH)_3$.

When dicarboxyphenylglyoxylic acid is heated at 240—260°, water, carbonic anhydride, and carbonic oxide are evolved; the residue contains, in addition to hemimellitic acid, two substances, one of which may be extracted by boiling water, and consists of *benzaldehydedicarboxylic acid*, $CHO\cdot C_6H_3(COOH)_2$; it forms colourless crystals, is readily soluble in water, melts at 175—178°, and combines with phenylhydrazine to form a hydrazone. The second compound is insoluble in water, has the composition $C_9H_4O_4$, and does not melt at 340°; on warming with phenylhydrazine and alcohol, it yields the hydrazone obtained from benzaldehydedicarboxylic acid, and is, therefore, probably the *dilactone* of this acid, $C_6H_3<\begin{matrix}COO\\ COO\end{matrix}>CH$.

Nitronaphthalic acid, on oxidation with alkaline permanganate, yields dicarboxynitrophenylglyoxylic acid. H. G. C.

Chrysene. By E. Bamberger and F. Chattaway (*Ber.*, **26**, 1745—1751).—Chrysenic acid, $C_{17}H_{12}O_2$ (Abstr., 1890, 1312), on distillation with lime under diminished pressure (40—50 mm.), yields a mixture of chrysoketone and a hydrocarbon which is identical with β-phenylnaphthalene (this vol., i, 522). The hydrocarbon obtained by Graebe (*Ber.*, **6**, 66; **7**, 782) by the distillation of chrysoquinone with soda-lime, is also identical with this product. Chrysene is

therefore a derivative of this hydrocarbon, and has the formula $\begin{matrix} C_6H_4\cdot CH \\ | \quad\quad \| \\ C_{10}H_6\cdot CH \end{matrix}$, chrysenic acid being probably β-phenylnaphthoic acid, $C_{10}H_6Ph\cdot COOH$ (compare next abstract). The CH=CH group of the hydrocarbon and the carboxyl of the acid are probably combined with the α-carbon atom of the naphthalene ring. A. H.

Picene. By E. Bamberger and F. Chattaway (*Ber.*, **26**, 1751—1754).—Picene melts at 350° (uncorr.), 364° (corr.), and has, therefore, a higher melting point than any other known hydrocarbon. It yields a quinone, $C_{20}H_{14}(CO)_2$, which behaves as an ortho-diketone, and an acid, $C_{21}H_{14}O_2$, which closely resembles chrysenic acid, and has, therefore, been named picenic acid. As this substance, on distillation with lime, yields $\beta\beta$-dinaphthyl, it follows that picenic acid is β-naphthylnaphthoic acid, $C_{10}H_7\cdot C_{10}H_6\cdot COOH$, whilst picene itself is $\beta\beta$-dinaphthylethylene, $\begin{matrix} C_{10}H_6\cdot CH \\ | \quad\quad \| \\ C_{10}H_6\cdot CH \end{matrix}$.

Picene is therefore the phenanthrene of the naphthalene series, and is closely related to chrysene (compare preceding abstract). Picene also furnishes a ketone, $(C_{10}H_6)_2CO$, obtained by distilling picenequinone with lead oxide; this corresponds with diphenylene ketone and chrysoketone, and, on reduction, gives rise to picenefluorene alcohol, $CH(C_{10}H_6)_2\cdot OH$, and picenefluorene, $CH_2(C_{10}H_6)_2$. The three hydrocarbons, picene, chrysene, and phenanthrene, therefore, resemble one another very closely, and may be converted by similar steps into their parent hydrocarbons, $\beta\beta$-dinaphthyl, β-phenylnaphthalene, and diphenyl. A. H.

American Oil of Turpentine. By J. H. Long (*J. Anal. Chem.*, **7**, 99—108).—The specific gravity and specific rotation of nearly 40 samples of oil of turpentine have been determined, including commercial products and specimens prepared in the manner described by the author, so as to exclude changes brought about by exposure to air or during distillation. It appears from these results that the oil collected from spruce trees is lævorotatory, $[\alpha]_D = -34{\cdot}828$; in two cases the rotation was greater than that observed by Tilden for pure australene, namely, $+29{\cdot}581$ and $+25{\cdot}114$ respectively. Exposure of the gum on the trees does not appear to lower the rotatory power of the product. Pinene is accompanied in the turpentine by a lævorotatory compound of higher boiling point, and the author suggests that this may possibly be the hitherto unknown lævorotatory cymene. On exposure to light during 20 days, commercial turpentine exhibits a slight increase in rotation; but no precautions were taken to exclude moisture, or even air. By the action of air, the specific rotation, specific gravity, and boiling point rise, and the turpentine becomes yellow. The compound formed by the action of sodium on commercial turpentine appears to be without effect on the rotatory power, since the latter is practically unchanged after the removal of the sodium compound. The rotatory power of the hydrochloride, $C_{10}H_{16}HCl$, was also determined, $= +7{\cdot}036$, that of the original

turpentine being +15·607, although the absence or otherwise of the lævopinene derivative was not proved; the results appear to show that the relationship in molecular rotatory power between compounds and their simple derivatives is fallacious (compare Flawitzky, *Ber.*, **15**, 5).

J. B. T.

Terpineol. By O. Wallach and F. Kerkhoff (*Annalen*, **275**, 103—110).—Bouchardat and Voiry (Abstr., 1887, 677) obtained terpineol in a solid crystalline form; the authors find that it melts at 35° and remains in superfusion for long periods. The terpenylphenylurethane, which it yields by combination with phenylcarbimide, melts at 113°. When terpineol is heated at 180—190° with potassium hydrogen sulphate, dipentene is the chief product; boiled with dilute sulphuric acid for an hour, it yields terpinene, cineole, terpinolene, and traces of dipentene; whilst if heated on the water-bath for seven hours with glacial acetic acid and a little dilute sulphuric acid, a small portion is converted into cymene and a little terpinene. When terpineol is boiled with 20 per cent. phosphoric acid, terpinene, cineole, and a small quantity of a hydrocarbon, yielding a solid bromide, are obtained. By boiling terpineol with a 50 per cent. solution of oxalic acid for five hours, the product consists mainly of terpinene, but small quantities of cineole and of terpinolene are also produced; when the boiling is of shorter duration, more terpinolene is obtained.

Experiments show that the bromine atoms are more readily removed from terpinolene tetrabromide when it is boiled with alcoholic potash than from the tetrabromides of limonene and dipentene.

A. R. L.

Dihydrocarveol. By O. Wallach, H. Kruse, and F. Kerkhoff (*Annalen*, **275**, 110—133).—Dihydrocarveol (Abstr., 1892, 499) is obtained by reducing either dextro- or lævo-carveol with sodium and alcohol; it rotates the plane of polarised light in the same direction as the carvol from which it is obtained. It has an odour recalling that of terpineol, boils at 224—225° under the ordinary pressure, and at 112° under 14 mm. pressure; it has a sp. gr. at 20° = 0·927, and a refractive power $[n]_D = 1·48168$. The *phenylurethane*, $C_{10}H_7O·CONHPh$, obtained from both optical antipodes, melts at 87°, whilst the *inactive* (*racemic*) modification melts at 93°. Dihydrocarveol is an unsaturated compound, and exhibits great similitude to terpineol. When dihydrocarveol is boiled with dilute sulphuric acid, terpinene is formed.

Dihydrocarvone, $C_{10}H_{16}O$, obtained by boiling a solution of dihydrocarveol in glacial acetic acid with an aqueous solution of chromic acid, can be purified by means of its *compound* with sodium hydrogen sulphite. It boils at 221—222°, and its vapour has the odour of menthone, or of carvol; its sp. gr. at 19° is 0·928, its specific refractive power $[n]_D = 1·47174$. It is dextro- or lævo-rotatory according as it originates from dextro- or lævo-dihydrocarveol. The optically active *oximes*, $C_{10}H_{16}·NOH$, melt at 88—89°, whilst the *inactive* (*racemic*) modification melts at 115—116°.

Dihydrocarvylamine, $C_{10}H_{17}·NH_2$, is the compound described by Goldschmidt (Abstr., 1887, 249 and 475) as carvylamine, and is best prepared by reducing carvoxime with sodium and alcohol; it

can also be obtained from carvol and ammonium formate (see Abstr., 1892, 499). The *phenylhydrocarvylthiocarbamide*,

$$C_{10}H_{17}\cdot NH\cdot CS\cdot NHPh,$$

obtained from the compound of either origin, melts at 125—126°, and the *acetyl* derivative, $C_{10}H_{17}\cdot NHAc$, at 132°. The *hydrochloride*, $C_{10}H_{17}NH_2,HCl$, melts at 190° with decomposition (see below), the *benzoyl* derivative at 181—182°, and the *phenylhydrocarvylcarbamide* at 191°. Dextro- and lævo-dihydrocarvylamine and their derivatives have similar properties. The inactive (racemic) *phenylhydrocarvylthiocarbamide* melts at 119°.

On heating dihydrocarvylamine hydrochloride, boiling the base with dilute sulphuric acid, heating it with potassium hydrogen sulphate, or warming the normal nitrite with water, terpinene, admixed with a small quantity of cymene, is obtained.

When a concentrated aqueous solution of dihydrocarvylamine hydrochloride is warmed with a solution of sodium nitrite, dipentene (inactive limonene) is formed, probably through the intermediary production of an alcohol; the conversion of carvol into limonene has therefore been accomplished. In the reaction last described, the formation of a nitrite which gave dihydrocarveol on hydrolysis with potash was also observed.

Terpineol and dihydrocarveol are therefore closely related, and appear to differ only in the positions of their hydroxyl groups. Terpineol is a tertiary alcohol, and dihydrocarveol a secondary alcohol.

A. R. L.

Oxidation of Terpene Derivatives. By O. WALLACH (*Annalen*, **275**, 145—183).—Carvol and dihydrocarveol are readily oxidised when shaken with potassium permanganate solution in the cold, and on adding sodium hydroxide and iodine to the filtered liquid, iodoform separates; if bromine instead of iodine is used, carbon tetrabromide is precipitated. Terpinol, limonene, and other terpene derivatives likewise yield carbon tetrabromide under similar treatment. When bromine is added to dilute solutions of dehydracetic and mesitonic acids containing alkali (an excess of alkali must in all cases be employed), carbon tetrabromide is obtained, and it is also formed by treating extremely dilute alkaline solutions of levulinic acid, mesitonic acid, and acetone with bromine. It is therefore suggested that the formation of carbon tetrabromide is brought about in compounds containing the acetyl group, when the dilution is such that the bromine can interact with the nascent bromoform, the latter being precipitated from more concentrated solutions. With compounds which, in relatively more concentrated solutions, give rise to the formation of carbon tetrabromide, it is concluded either that no ready-formed acetyl group is present, but that such a complex is produced during the reaction, which is sufficiently prolonged to favour the precipitation of carbon tetrabromide, or that the compound has an atomic configuration which renders it capable of directly forming carbon tetrabromide.

When terpineol is carefully oxidised in the cold with potassium permanganate, the aqueous solution gives the iodoform and carbon

tetrabromide reactions, and it therefore seemed likely that the product was a ketonic acid. It proves, however, to be an indifferent *compound*, $C_{10}H_{20}O_3$, and, in view of Wagner's investigations, may be a trihydroxyterpine; it crystallises from alcoholic ether in transparent crystals, melts at 121—122°, boils at 170—180° (11 mm.), and is almost insoluble in ether. When this substance is further oxidised with chromic acid and dilute sulphuric acid, it is converted into a compound $C_{10}H_{16}O_3$, which crystallises from water in monoclinic pyramids, melts at 62—63°, and boils at about 330°.

Dihydrocarveol, on oxidation, behaves in a manner similar to terpinol; the product has not yet been obtained in the crystalline condition. On oxidation with potassium permanganate, carvol yields a neutral *compound*, $C_{10}H_{12}O_5$, soluble in water, and two *acids* melting at about 185° and 100° respectively.

The resemblance of the reactions of fenchone and camphor has already been noted (Abstr., 1891, 1086; 1892, 1236). It is now found that when fenchone is gently heated with phosphoric anhydride (under which circumstances camphor yields cymene) it is converted into *metacymene* (*metamethylisopropylbenzene ?*); it boils at 175—176°, has a sp. gr. at 20° = 0·862, and a specific refractive power $[n]_D$ = 1·49222. On oxidation with potassium permanganate, it yields an unsaturated acid, $C_{10}H_{10}O_2$, which is volatile with steam, and melts at 99°, also an *acid* which is not volatile with steam, melts at 123—124°, and has the composition of a hydroxypropylbenzoic acid; on oxidation with dilute nitric acid, metatoluic acid is formed. The production of isocymene has been observed from other terpene derivatives, but its formation from camphor and zinc chloride (Armstrong and Miller, Abstr., 1884, 44) is probably due to a secondary reaction.

Methylheptylene ketone (Abstr., 1893, i, 106) is obtained somewhat less readily from α-thujaketonic acid than from the β-acid; this ketone has probably the constitution $CHMe_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}COMe$. It is converted into dihydro-ψ-cumene, C_9H_{14}, when heated on the water-bath with zinc chloride; the latter boils at about 160°, has a sp. gr. at 19° = 0·844, and a specific refractive power $[n]_D$ = 1·47194. When the methylheptylene ketone is reduced with sodium and alcohol, an unsaturated *alcohol* (see also *loc. cit.*), boiling at 185—187°, is formed; it has a sp. gr. at 21° = 0·848, and a specific refractive power = 1·4458. It combines with bromine and hydrogen bromide, and is probably represented by the constitutional formula

$$CHMe_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH.$$

When the alcohol is heated with zinc chloride or dilute sulphuric acid, it yields, instead of a hydrocarbon, an isomeric saturated *oxide*, closely resembling cineole, and having the odour of peppermint; it boils at 149—151°, has a sp. gr. at 20° = 0·847, and a specific refractive power $[n]_D$ = 1·42693; its constitution is probably

$$CHMe_2{\cdot}CMe\begin{<}{CH_2{\cdot}CH_2}\\{O-CHMe}\end{.}$$

The isomerism of α- and β-thujaketonic acids needs further investi-

gation. Semmler (this vol., i, 108) believes them to be stereoisomerides, but the author gives reasons for not accepting the constitutional formula proposed by him. Accepting the above formulæ for methylheptylene ketone, the constitution of the thujaketonic acids is most probably $COMe{\cdot}CH_2{\cdot}CH{:}C(CHMe_2){\cdot}CH_2{\cdot}COOH$.

When the ketone (methylhexylene ketone), $C_8H_{14}O$, boiling at 173—174° (Abstr., 1890, 1314), is treated with sodium and alcohol, an unsaturated alcohol, $C_8H_{13}{\cdot}OH$, is obtained; this boils at 174—176°, has a sp. gr. = 0·85, and a specific refractive power $[n]_D = 1{\cdot}44889$. When the alcohol is warmed with dilute sulphuric acid, it is converted into an isomeric oxide, which boils at 127—129°, has a sp. gr. 0·85, and a specific refractive power $[n]_D = 1{\cdot}4249$. The analogy of the compounds $C_9H_{18}O$ and $C_8H_{16}O$ is therefore complete.

When bromine is added to thujone diluted with light petroleum, a tribromo-derivative, $C_{10}H_{13}Br_3O$, is formed; it crystallises in monoclinic plates, melts at 121—122° with decomposition, and slowly undergoes decomposition at the ordinary temperature. The author has obtained the same compound from Semmler's tanacetone (*loc. cit.*), and thereby proves this chemist's observation that tanacetone and thujone are identical.

When thujone is treated with a solution of bleaching powder, or of alkaline hypobromite, a saturated *bibasic acid*, $C_{10}H_{16}O_4$, which melts at 146—147° with decomposition, is formed, together with a smaller amount of Semmler's liquid acid (tanacetogenic acid). Semmler has privately informed the author that he has since obtained the same result.

The fraction of thuja oil boiling above 220° yields an inactive *oxime*, melting at 93—94°; it is probably identical with inactive carvole. A. R. L.

The Constitution of Camphor. By P. Cazeneuve (*Bull. Soc. Chim.* [3], **9**, 38—45).—This paper discusses the evidence generally for the constitution of camphor, and concludes in favour of Kekulé's formula as modified by Haller. W. T.

Bromocamphoric Anhydride and Camphoric acid. By O. Aschan (*Ber.*, **26**, 1639—1645).—Bromocamphoric anhydride, when reduced with zinc-dust and acetic acid, yields mainly camphoric anhydride (m. p. 217—218°), which is precipitated from the acetic solution by the addition of water. The filtrate contains a camphoric acid, which crystallises in tufts of slender needles, melts at 120—125°, and when crystallised three or four times from dilute alcohol, is converted into a modification which crystallises in rhombohedra or plates, melts at 172—173°, and is probably isocamphoric acid. The author was unable to isolate ordinary camphoric acid from the product of the reduction of bromocamphoric anhydride (Rupe and Maull, this vol., i, 524).

When camphoric chloride is treated with 2, 3, or 4 atoms of bromine, only 1 atom of bromine is introduced into the molecule, and by treating the product with water or formic acid, bromocamphoric anhydride is obtained. The substance prepared in this way is crystallo-

graphically identical with that prepared from camphoric acid or its anhydride.

Bromocamphoric anhydride, when treated with alcoholic potash, is converted into camphanic acid; when heated with aniline on the water-bath, it yields phenylamidocamphoric anhydride; when boiled with potassium acetate and acetic acid, it gives a quantitative yield of camphanic acid; and, when melted with potassium acetate, it yields acetic anhydride and potassium camphanate. E. C. R.

Ethyl Hydrogen Camphorate. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, **12**, 23—25).—This substance, obtained by adding sodium ethoxide to an alcoholic solution of camphoric anhydride, or by passing gaseous hydrogen chloride into an alcoholic solution of the acid, has been obtained in rhombic prisms, melting, in the first case, at 46—47·5°, in the second at 47—48·5°; previously it was known only as an oil. C. F. B.

Substituted Isoimides of Camphoric acid. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, **12**, 12—22).—*Camphormethylimide*, prepared by heating camphormethylamic acid, forms colourless crystals, melts at 40—42°, and boils at 270°. *Camphorbenzylimide*, prepared by heating benzylammonium camphorbenzylamate, forms colourless crystals melting at 58—62°.

When substituted camphoramic acids are heated at 80° with acetic chloride (3 parts), or at 100—110° with phosphorus oxychloride (2 parts), substances isomeric with the imides are obtained. These *isoimides* remain as oils when the product is treated with carbon bisulphide, to remove the excess of chloride, and can then be purified by solution in ether, precipitation as hydrochloride by means of gaseous hydrogen chloride, decomposition of the hydrohloride with soda, and extraction of the isoimide with ether. *Camphormethylisoimide* forms small, tabular crystals which melt at 134—136°, and at a higher temperature are transformed into the imide. Water regenerates the amic acid; methylamine gives *camphordimethyldiamide*, $C_8H_{14}(CONHMe)_2$, as a crystalline powder melting at 244—247°. *Camphorethylisoimide* forms tables melting at 80—82°; *camphorbenzylisoimide* small tables melting at 63—66°. Isoimides of other orthodicarboxylic acids could not be prepared, except in the case of phthalic acid, of which an isoimide was probably obtained, but not in a pure state.

The substituted camphorimides are usually assumed to have the constitution $C_8H_{14}<^{CO}_{CO}>NR$, and the structure of the isoimides is hence probably represented by $C_8H_{14}<^{C(NR)}_{CO\text{—}\!\!\!\text{—}}>O$. If this is so, then phthalisoimide will be the intermediate compound discussed in this vol., i, 268, and should therefore yield orthocyanobenzoic acid when treated with ammonia; this the above-mentioned impure phthalisoimide actually does. Similarly, it was found possible to obtain camphorisoimide itself, although not in a pure state, and to convert it, by means of ammonia, into an acid, $CN{\cdot}C_8H_{14}{\cdot}COOH$.

C. F. B.

Action of Phenylhydrazine on Camphoric Anhydride and the Ethereal Salts of Camphoric acid. By C. FRIEDEL and A. COMBES (*Bull. Soc. Chim.* [3], **9**, 27—30).—Camphoric anhydride reacts with phenylhydrazine when heated with it for a long time on the water-bath or for a few minutes at 180—200°, yielding colourless crystals, insoluble in cold, slightly soluble in hot water, melting at 119°, and having the composition $C_{16}H_{20}N_2O_2$. There is no action at the ordinary temperature.

Diethylic camphorate is not acted on by phenylhydrazine when boiled therewith for several hours. Monethylic camphorate, prepared by the direct etherification of camphoric acid by alcohol and hydrogen chloride, yields the compound $C_{16}H_{20}N_2O_2$, as Haller has shown for the methylic salt (compare Brühl and Braunschweig, this vol., i, 277); whereas the monethylic camphorate, prepared by partial hydrolysis of the diethylic salt, is not acted on. Hence the dicarboxylic formula for camphoric acid must be rejected. The difference of the reaction with phenylhydrazine in the two cases is easily explained if the substance fusing at 119° be represented as $CHPr<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO\\ N\cdot NHPh\end{matrix}$. The production of increasing quantities of camphorimide (m. p. 245°), and of benzene when the mixture of phenylhydrazine and camphoric anhydride is maintained for some minutes at 200°, renders the formula given more probable if camphoric acid be admitted to be a ketohydroxymonocarboxylic acid (see also Brühl, Abstr., 1892, 1100; and Friedel, Abstr., 1892. 500).

W. T.

Preparation of Cantharidin. By E. DIETERICH (*J. Pharm.* [5], **27**, 375—377; from *Helfenberger Ann.*, 1892, 1).—Coarsely powdered cantharides (1000 grams) are placed in a porcelain vessel, and a mixture of ethylic acetate (1500 grams; sp. gr. = 0·902) and sulphuric acid (20 grams; sp. gr. = 1·838) is added, the whole stirred thoroughly, and left for two days. (The object of the sulphuric acid is to decompose a compound of cantharidin contained in the insects.) Barium carbonate (40 grams) is then added, and stirred in, and the whole is extracted with ethylic acetate in a reflux extraction apparatus. The residue, after distilling off the ethylic acetate from the extract, is left for eight days in a porcelain capsule to allow the cantharidin to crystallise. Fats are removed by boiling with light petroleum (200 grams; sp. gr. = 0·740), and washing the residue two or three times with hot light petroleum (30 grams each time). Resins are now removed by pulverising the residue, warming with alcohol of 90° (300 grams), setting aside, pouring off the liquid the next day, and washing the residual crystals with alcohol (20 grams) and then with ether (20 grams; sp. gr. = 0·720). The cantharidin is now sufficiently pure for making plasters; to further purify it, it may be heated (15 grams) for two hours at 40—50° with ethylic acetate (150 grams) and animal charcoal (1 gram), and the solution filtered and allowed to crystallise. The yield varies from 0·3 to 1·03 per cent. of the insects taken.

C. F. B.

Scoparin. By G. Goldschmiedt and F. v. Hemmelmayr (*Monatsh.*, **14**, 202—222).—This substance, together with sparteïn, was discovered by Stenhouse in the aqueous extract of *Spartium scoparium*. In order to purify it, it was repeatedly dissolved in boiling water, from which it separates, on cooling, as a gelatinous mass, and crystallised from 70 per cent. alcohol. It forms nodular aggregates of small, yellow needles, melts at from 202° to 219°, accordingly as it is heated slowly or quickly, and seems to have the composition $OH{\cdot}C_{19}H_{16}O_8{\cdot}OMe + 5H_2O$ (Stenhouse, $C_{21}H_{22}O_{11}$). It reduces Fehling's solution, and gives, with ferric chloride, a violet-blue coloration which quickly becomes dark-brown, or is changed to yellowish-brown by sodium carbonate. A *barium* derivative, $(C_{20}H_{19}O_{10})_2Ba + 2H_2O$, was obtained by boiling an aqueous solution of scoparin with barium carbonate. When heated with hydriodic acid, scoparin yields 1 mol. of methylic iodide, and at the same time loses 1 mol. of water, giving a substance, $C_{19}H_{14}O_8$, which forms a bright yellow, amorphous powder, becomes dark at 175°, and melts with decomposition above 200°. It yields a *monacetyl derivative* forming nearly white crystals, melting at 230—236° when still impure, and a *monethyl derivative* crystallising in tiny, bright yellow needles melting with decomposition at 272°. It seems not to be a glucoside, for when boiled with dilute sulphuric acid, no sugar could be detected in the solution; an insoluble, brownish-yellow substance, $C_{20}H_{16}O_8 + 2\frac{1}{2}H_2O$ (?), was, however, formed. When scoparin is boiled with absolute alcohol, it is converted into Stenhouse's "apparently allotropic" modification; this forms a yellow, crystalline powder, melts at 235°, and seems to have the same percentage composition as scoparin itself.

C. F. B.

Urson. By W. H. Gintl (*Monatsh.*, **14**, 255—269).—This substance occurs, together with arbutin, in the leaves of the red bear berry (*Arbutus uva ursi*). It has the constitution $C_{30}H_{48}O_3 + 2H_2O$, possibly $O<\begin{matrix}-C_{15}H_{24}-\\ C_{15}H_{23}(OH)\end{matrix}>O$ containing two sesquiterpene residues, and melts at 263—266°, not, as Hlasiwetz says, at 198—200°. When it is dissolved in acetic anhydride, and concentrated sulphuric acid added to the solution when cold, a red coloration is produced which rapidly becomes violet, then blue, and finally green; if a drop of water is added immediately after the sulphuric acid, the red colour at once changes to green. Urson does not react with hydroxylamine or phenylhydrazine; it contains no methoxyl group; but it does contain an hydroxyl group, for it yields a *monacetyl derivative* which forms white needles melting at 264°, and a *monobenzoyl derivative*, as a yellowish, amorphous powder, melting at 214°. The action of bromine, permanganate, chromic acid, and fused potash was also studied, but no very definite results were obtained. When reduced with hydriodic acid and phosphorus at 360°, or, better, when distilled with zinc-dust in a stream of hydrogen, ursen yields small quantities of a substance, $C_{15}H_{24}$, probably a sesquiterpene, which boils at 256—267°, is feebly dextrorotatory, and gives a red coloration with

strong sulphuric acid, and a dark-brown one with acetic anhydride and a drop of sulphuric acid. C. F. B.

New Naturally-occurring Nitrogenous Organic Acid. By F. KLINGEMANN (*Annalen*, **275**, 89—91).—Stahlschmidt (*Annalen*, **187**, 177; **195**, 365) obtained an acid $(C_9H_7O_3)_n$, which he named polyporic acid, from a certain fungus occurring on diseased oaks. This fungus was perhaps *Polyporus igniarus*, and it seems probable that the acid was not a normal constituent but a pathogenic one. The author finds that *Polyporus igniarus* contains an acid which differs from polyporic acid, but may, perhaps, under certain conditions, be convertible into it. The new acid dissolves in alkalis with a deep brown colour, and on analysis gives values agreeing best with the formula $C_{36}H_{39}N_3O_{16}$. A. R. L.

The Basic Properties of Pyrroline Derivatives. By G. CIAMICIAN and C. U. ZANETTI (*Ber.*, **26**, 1711—1714).—Pyrroline, 1-ethylpyrroline, 2 : 5-dimethylpyrroline, and other homologues of pyrroline dissolve in hydrochloric acid, and the solutions give precipitates with the reagents generally used in precipitating alkaloïds, as, for example, phosphomolybdic acid; particularly well-characterised are the *ferrocyanides* of *pyrroline* and *1-ethylpyrroline*,

$$C_4NH_8,H_4Fe(CN)_6 \text{ and } C_4NH_4Et,H_4Fe(CN)_6.$$

An alkali does not, however, regenerate the original pyrroline from these compounds, but only resinous substances, probably polymerides. On the other hand, ketonic derivatives of pyrroline do give salts from which the original substance may be regenerated. Of these salts there were prepared and analysed the *hydrochloride* and *aurochloride* of *2 : 5-dimethyl-3-acetylpyrroline* and of *2 : 4-dimethyl-5-acetylpyrroline*; and the *aurochloride* of *2 : 4-dimethyl-3 : 5-diacetylpyrroline* and of *2 : 5-dimethyl-3 : 4-diacetylpyrroline*, as well as the *hydrobromide* of this last substance, and a *dibromo-additive compound* of the hydrobromide. Pyrrolines, although they do thus form salts, are but feebly basic; this is, however, no argument for their containing *penta*valent nitrogen, for many other compounds, in which Bamberger does not hesitate to assume the presence of *tri*valent nitrogen, have equally feeble basic properties. C. F. B.

Piperidine Bases of the β-Series. By C. STOEHR (*J. pr. Chem.* [2], **48**, 17—18).—The following additions are to be made to the author's previous paper on this subject (Abstr., 1892, 628):—*β-Methylpiperidine platinochloride*, $(C_6H_{13}N)_2,H_2PtCl_6$, crystallises in long, red prisms, dissolves sparingly in water, and melts at 207° with much evolution of gas; its crystallography is given (compare Hesekiel, Abstr., 1885, 812). *β-Ethylpiperidine aurochloride*, $C_7H_{15}N,HAuCl_4$, forms lustrous, rhombohedral crystals, whose measurements are given. A. G. B.

Conversion of the Indoles into Quinolines. By A. FERRATINI (*Ber.*, **26**, 1811—1815).—Both the trimethyltetrahydroquinoline and

the trimethyldihydroquinoline obtained from indole (this vol., i, 227) are decomposed by phosphorus and hydriodic acid at 230° yielding methylic iodide and dimethyltetrahydroquinoline, which can be isolated by means of its crystalline hydriodide. The free base boils at 234—235°, and yields a hydrochloride of the composition $C_9NH_9Me_2,HCl$, which melts at 198—199°. When this substance is distilled over zinc-dust, hydrogen is evolved and a yellow oil produced. A small amount of 2′ : 3′-dimethylindole is formed by the distillation, and is removed by treating the oil with hydrochloric acid, in which the indole compound is insoluble, whilst unaltered dimethyltetrahydroquinoline can be removed by the action of nitrous acid. The base thus prepared boils at 263—266°, and is identical in composition and properties with 2′ : 4′-dimethylquinoline. When an indole is converted into a quinoline derivative, then, by the action of methylic iodide, the carbon atom which enters the pyrroline ring takes up the 3′- or meta-position relatively to the nitrogen atom. The tetrahydro-2′ : 4′-dimethylquinoline obtained from indole is, however, not identical with that prepared synthetically. The explanation of this remarkable circumstance may perhaps be found in the fact that 2′ : 4′-dimethyltetrahydroquinoline contains two asymmetric carbon atoms, $C_6H_4<\begin{matrix}CHMe\cdot CH_2\\ NH-CHMe\end{matrix}$, so that it is possible that the two known 2′ : 4′-dimethyltetrahydroquinolines are stereo-isomerides derived from the same dimethylquinoline. A. H.

Constitution of Cycloïd Systems. By W. Marckwald and others (*Annalen*, **274**, 331—376).—The author has previously brought forward certain facts (Abstr., 1890, 1004) connected with Skraup's quinoline synthesis which are only to be explained by the adoption of Kekulé's benzene formula; he maintains that this formula has been disproved neither by v. Baeyer nor by Zincke. Representing naphthalene by Erlenmeyer's and Graebe's formula, and quinoline by Körner's formula, the positions 1 : 2 and 3 : 4 are completely different from the position 2 : 3, whereas the formulæ of Claus and of Bamberger do not indicate such a difference in these positions, it being in the latter cases merely a question of relative situation. On these lines, the following experiments are in accordance with Erlenmeyer and Graebe's formula for naphthalene and Körner's formula for quinoline; they also show that the existence of para-bonds in benzene is extremely improbable.

Dinitrotoluenesulphonic acid [$Me : (NO_2)_2 : SO_3H = 1 : 2 : 6 : 4$] does not yield the diamido-compound on reduction with ammonium sulphide as Schwanert states (this Journal, 1877, ii, 612), but under these circumstances the *nitro-amidosulphonic acid* is formed; this crystallises in delicate needles, and is sparingly soluble in water. The *potassium* and *calcium* salts are anhydrous; the *barium* salt crystallises with $2\frac{1}{2}H_2O$, and the *silver* salt with $\frac{1}{2}H_2O$. On reducing the dinitro-compound with tin and hydrochloric acid, the diamidotoluenesulphonic acid agreeing with Schwanert's description is formed. It yields by Skraup's reaction 1-*methyl*-2-*amidoquinoline*-4-*sulphonic*

acid, which crystallises from water in yellowish-red needles containing $1H_2O$; the *sodium* and *calcium* salts form yellow, anhydrous needles, the *barium* and *silver* salts crystallise with $2H_2O$, and the *copper* salt crystallises with $1H_2O$.

1 : 2'-*Dimethyl*-2-*amidoquinoline*-4-*sulphonic acid* is obtained from the above diamidotoluenesulphonic acid by the Doebner-Miller reaction (paraldehyde and hydrochloric acid); it crystallises from hot water in bright yellow, thick needles containing $2H_2O$. The *sodium*, *potassium*, *calcium*, *silver*, and *lead* salts are anhydrous; the *barium* salt crystallises with $4H_2O$, and the *copper* salt with $1H_2O$. The two above-described amidoquinoline derivatives remain unaltered when further treated either by the Skraup or the Doebner-Miller reactions because, according to the author, single bonds exist between the 2 : 3-positions in each (Körner's formula).

Dinitroparatoluic acid [Me : $(NO_2)_2$: COOH = 1 : 2 : 6 : 4] (Abstr., 1892, 177) crystallises with 1 mol. H_2O, and forms a *sulphate* which is sparingly soluble in water, and crystallises with 3 mols. H_2O. 1-*Methyl*-2-*amidoquinoline*-4-*carboxylic acid* is obtained from the diamidotoluic acid by Skraup's reaction; it forms sulphur-yellow crystals containing $1\frac{1}{2}H_2O$, and decomposes without melting at 270°; the *silver* salt, the *hydrochloride*, the *platinochloride*, and other salts were prepared; the *acetyl* derivative, $COOH{\cdot}C_9NH_4Me{\cdot}NHAc$, forms bright grey, pulverulent crystals, does not melt at 300°, and is hydrolysed into the amido-compound by cold acids. When the last-described methylamidoquinolinecarboxylic acid is distilled, 1-*methyl*-2-*amidoquinoline* passes over at 304°; it crystallises in white prisms, melts at 129°, and remains unaltered when treated by Skraup's reaction; the *picrate*, *chromate*, and *platinochloride* were prepared.

1 : 2'-*Dimethyl*-2-*amidoquinoline*-4-*carboxylic acid* is obtained by treating the above-mentioned diamidoparatoluic acid by the Doebner-Miller reaction; it forms small, golden-yellow crystals, and decomposes at a high temperature without melting; the *silver* salt, the hydrochloride and other salts, as well as the acetyl derivative, are described; 1 : 2'-*dimethyl*-2-*amidoquinoline* is obtained by distilling the dimethylamidoquinolinecarboxylic acid; it forms long, colourless, lance-shaped crystals, and melts at 104°; the *picrate*, *platinochloride*, and *dichromate* were prepared.

Benzoparaphenanthroline, $\begin{matrix} CH{-}N \\ | \\ CH{\cdot}CH \end{matrix}\!\!>\!C_{10}H_4\!<\!\!\begin{matrix} CH{\cdot}CH \\ | \\ N{-}CH \end{matrix}$, is prepared by treating 1 : 4-diamidonaphthalene by Skraup's reaction; it crystallises in transparent, microscopic tables or needles, and melts at 160°; the *picrate* melts at 256°.

Paraphenylenediimidopropyl methyl ketone, $C_6H_4(N{:}CMe{\cdot}CH_2{\cdot}COMe)_2$, is obtained by heating paraphenylenediamine with acetylacetone (2 mols.) at 120°. It crystallises from dilute alcohol in yellowish, nacreous leaflets, melts at 175°, and is decomposed into its components when heated with dilute acids or alkalis. All attempts, such as treating it with concentrated sulphuric acid in the cold or at 100°, or by heating it alone, failed to produce a quinoline derivative.

Metaphenylenediimidopropyl methyl ketone, prepared from metaphenylenediamine and acetylacetone, forms bright yellow, lance-shaped crystals, and melts at 135°; it is converted into *amidodimethylquinoline* [$NH_2 : Me_2 = 4 : 2' : 4'$ or $2 : 2' : 4'$] when heated with concentrated sulphuric acid at 100°, or when boiled with glacial acetic acid; the new compound is an oil boiling above 300°, and forming a hydrate, with $2H_2O$, which crystallises in yellowish needles; when heated for a long time at 120°, it yields a resinous mass from which an anhydrous modification is obtained on crystallisation from light petroleum; it melts at 94—100°, and is reconverted into the oily modification on exposure to the air. The *salts* of the base are of a yellow to red colour; the *picrate* melts at 215—217°; the *acetyl* derivative forms yellowish needles. and melts at 212°.

Phenyldimethylquinolinethiocarbimide, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_{11}NH_{10}$ is obtained by boiling together alcoholic solutions of the amidodimethylquinoline and phenylthiocarbimide; it is a yellow, crystalline powder, melts at 173—174°, and has only weak basic properties; the corresponding *paratolyl* derivative, $C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{11}NH_{10}$, melts at 142°.

When the last-described amidodimethylquinoline is treated with acetylacetone, a syrupy compound, $C_{11}NH_{10}{\cdot}NMe{\cdot}CH_2Ac$, is formed, and this, on being heated with concentrated sulphuric acid, is reconverted into the amidodimethylquinoline. When, however, the amidodimethylquinoline is treated by Skraup's reaction, *dimethylphenanthroline*, $\begin{matrix}CH{-}N\\ |\\ CH{\cdot}CH\end{matrix}\!\!>\!C_9NH_3Me_2$ (3 or 1 : 1 : 3 / 4 or 2), is obtained; it forms white crystals, and melts at 106—107°; and the *picrate* forms lustrous, yellow needles, and commences to decompose at 230° without melting.

A. R. L.

Oxidation of Parahydroxyquinoline. By O. Rosenheim and J. Tafel (*Ber.*, **26**, 1501—1513).—*Pyridylglycerolcarboxylic acid*, $COOH{\cdot}C_5NH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, is prepared by the action of calcium hypochlorite in aqueous solution at 0° on parahydroxyquinoline; it is crystalline, and sparingly soluble in cold water, but dissolves readily on heating, and gives a yellow coloration with ferric chloride. The *calcium* and *silver salts* are crystalline; the *potassium salt* forms a syrup; the *lead* and *copper salts* are sparingly soluble. The acid is not acted on by nitrous acid, or hydroxylamine, or by boiling it with water or dilute (10 per cent.) sulphuric acid.

On treating the calcium salt with hydrochloric acid, the *acid lactone*, $C_9H_7NO_5$, is obtained; it crystallises from water in large, thin plates, melts at about 210° with decomposition, and gives a yellow coloration with ferric chloride. The same compound is also formed by the action of calcium hypochlorite on acetylparahydroxyquinoline, showing that the resolution of the quinoline ring occurs at the position of the hydroxyl group. The *ammonium salt* is crystalline; the *calcium* and *silver salts* are deposited in needles; the *copper*, *zinc*, *cadmium*, *mercury*, and *lead salts* are sparingly soluble and crystalline. The *ethylic salt* is deposited from water in groups of colourless

needles, and melts at 135—136° with evolution of gas. The *methylic salt* crystallises in prisms melting at 152°. The *acetyl derivative* is deposited from water in long, thick needles, melts at 177°, and gives no coloration with ferric chloride. The lactonic acid is scarcely acted on by nitric acid or potassium permanganate, but yields quinolinic acid on oxidation with sulphuric acid and potassium dichromate.

On heating the lactonic acid with ammonia in a sealed tube for two hours at 150—160°, and treating the crystalline product with sulphuric acid, an acid, $C_9H_6N_2O_3$, is formed which is deposited from glacial acetic acid in colourless, paper-like masses, darkening at 302°, melting at 321°, and giving a yellowish-red coloration with ferric chloride. This acid appears to be the analogue of isocarbostyril-carboxylic acid, and may perhaps therefore have the formula $C_5NH_3<\begin{matrix}CO\cdot NH\\ CH{:}C\cdot COOH\end{matrix}$; its formation indicates that pyridylglycerol-carboxylic acid lactone is probably a δ-lactone. On heating the imido-acid above its melting point, carbonic anhydride is evolved, and a crystalline compound sublimes, which is insoluble in alkalis, and melts at 236—238°.

α-Acetopyridine-β-carboxylic acid (*α-acetonicotinic acid*),

$$C_5NH_3Ac\cdot COOH,$$

is prepared by heating pyridylglycerolcarboxylic acid lactone with 5—6 parts of water in a sealed tube at 140°; it crystallises from water in small needles, melts at 127°, and gives no coloration with ferric chloride. The *potassium* and *ammonium salts* are readily soluble and crystalline; the *silver* and *mercurous salts* are sparingly soluble. The *ethylic salt* is an oily liquid, but forms a *hydrochloride*, crystallising in colourless plates which melt at 133—134°.

Acetonicotinic acid oxime anhydride, $C_5NH_3<\begin{matrix}CO\cdot O\\ -CMe=\end{matrix}>N$, is obtained by the action of hydroxylamine hydrochloride on the acid, and crystallises in long, slender needles; it melts at 171°, and dissolves in alkalis or in concentrated hydrochloric acid.

Acetonicotinic acid phenylhydrazone anhydride, $C_5NH_3<\begin{matrix}CO-NPh\\ CMe{:}N\end{matrix}$, is formed from phenylhydrazine hydrochloride and acetonicotinic acid, and crystallises from alcohol in colourless needles melting at 121°. The compound dissolves in concentrated mineral acids with a yellow colour, but is stable towards alkalis.

Acetonicotinic acid is scarcely affected by potassium permanganate even on heating, but by treatment with nitric acid, quinolinic acid is formed. J. B. T.

Isomerides and Congeners of "Analgen," Ethoxy-4-benzoylamidoquinoline. By G. N. Vis (*J. pr. Chem.* [2], **48**, 24—30).—"Analgen" is the trade name for ethoxy-4-benzoylamidoquinoline, a compound employed as an antineurotic. This substance is made from 1-ethoxynitroquinoline (Abstr., 1892, 1104) by reducing it to the amido-derivative by means of iron, and benzolysing by the Schotten-

Baumann method. It crystallises from alcohol, in which it dissolves sparingly; it is insoluble in water, but dissolves in acids, being a feeble base; it cannot be hydrolysed by alkalis or dilute acids. In the organism, analgen is partly entirely broken down and partly decomposed with liberation of ethoxyamidoquinoline, which forms a red-coloured urate in the urine.

Dinitro-1-*methoxyquinoline* is best prepared by nitrating methoxyquinoline sulphate; in properties it is very similar to the corresponding ethoxy-derivative (*loc. cit.*). 1-*Methoxy*-4-*nitroquinoline* crystallises as its nitrate from the filtrate from the preceding compound; this base melts at 151·5° and dissolves in hot alcohol, but not in water. When reduced in hydrochloric acid solution, it yields the corresponding *amido*-derivative, which crystallises from alcohol in yellow needles melting at 155—156°, and from water in crystals containing $1H_2O$ and melting at 76°.

1-*Methoxy*-4-*acetamidoquinoline* is prepared by treating the amide which has just been described with glacial acetic acid; it crystallises at first in needles, but these soon change into octahedral crystals; the crystals from an aqueous solution contain $1H_2O$. It melts at 179°. When it was administered to a dog, it was found to have, in great measure, passed through the system unchanged.

1-*Methoxy*-4-*benzoylamidoquinoline* was prepared, in a manner analogous to the ethoxy-derivative; it crystallises in white needles, melts at 268—269°, and dissolves in hot alcohol. Its salts are easily soluble.

3-*Ethoxy*-4-*nitroquinoline*, made by nitrating 3-ethoxyquinoline (b. p. 291°), crystallises in yellow needles; it is practically insoluble in water and has a sweet taste, whereas the 1-derivative is bitter. The *platinochloride* forms orange needles; the *methiodide* crystallises in orange-coloured prisms, and melts at 205° with decomposition.

3-*Ethoxy*-4-*amidoquinoline*, prepared by reducing the nitro-derivative, crystallises with $1H_2O$ in yellow needles which melt at 76°; the dry compound melts at 115—116°. It dissolves in hot alcohol and hot water. The *acetamido*-derivative crystallises in white laminæ, melts at 163—163·5°, and dissolves in hot water. The *benzoylamido*-derivative forms white crystals, melts at 144°, and is fairly soluble in water. The acid radicle is eliminated from each of these two derivatives in the system.

By diazotising the amido-derivative and treating the diazo-compound with cuprous bromide, 3-*ethoxy*-4-*bromoquinoline* was prepared; this crystallises in long, lustrous needles, melts, when dry, at 80—81°, and dissolves in hot alcohol; the *hydrochloride* forms sparingly soluble, yellow needles, and melts at 235°. The same ethoxybromoquinoline was prepared by treating 3-hydroxy-4-bromoquinoline with caustic soda and ethylic bromide, and thus the 4-position of the bromine atom and *pari passu* of the original nitro-group was verified.

A. G. B.

New Synthesis of Isoquinoline. By C. Pomeranz (*Monatsh.*, 14, 116—119).—Isoquinoline is formed when benzaldehyde is mixed with amidoacetal, $NH_2{\cdot}CH_2{\cdot}CH(OEt)_2$, the mixture dried with potassium carbonate, and heated for half an hour at 100—120° with 3—4 times its weight of strong sulphuric acid.

C. F. B.

A New Synthesis of Isoquinoline. By A. Bischler and B. Napieralski (*Ber.*, **26**, 1903—1908).—When an acidic derivative, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CRO$, of ω-phenylethylamine is heated with phosphorus pentoxide or zinc chloride, it is condensed to a substance that is doubtless a dihydroisoquinoline, $C_6H_4<\begin{matrix}CH_2{\cdot}CH_2\\ CR:N\end{matrix}$, although a satisfactory proof of this has not yet been obtained. The yield is poor. Phosphorus pentachloride does not effect this condensation; an imidochloride is formed which undergoes no further change.

ω-Phenylethylamine is obtained by reducing phenylacetoxime with sodium amalgam in alcoholic solution kept acid with acetic acid; it is a colourless liquid boiling at 197—198° under 725 mm. pressure. The *acetyl derivative* (*phenylethylacetamide*) forms nodular aggregates of white needles, melts at 42—44°, and boils at 305—306° under 725 mm. pressure; it yields by condensation 1′-*methyldihydroisoquinoline* as a yellow oil boiling at 237—242°, the *platinochloride* of which forms yellow crystals. The *benzoyl derivative* (*phenylethylbenzamide*) forms white plates melting at 113—114°; by condensation, it yields 1′-*phenyldihydroisoquioline*, which was obtained only as an impure oily product; this, however, yields an orange-coloured, crystalline *platinochloride* melting at 194—195°. The *formyl derivative* (*phenylethylformamide*) is a colourless oil boiling at 205° under 15 mm. pressure and, under the ordinary pressure at 300° with partial decomposition; it decomposes when an attempt is made to condense it to dihydroisoquinoline. C. F. B.

Isoquinoline Derivatives. By P. Fortner (*Monatsh.*, **14**, 146—164).—When isoquinoline is dissolved in strong nitric acid and the solution added to a mixture of strong sulphuric and fuming nitric acids, and heated on the water-bath, *nitroisoquinoline* [$NO_2 : N = 1 : 2'$ or $4 : 2'$] with $1H_2O$ is formed, and may be separated by adding potash; it crystallises in long, fine, silky, faintly yellowish needles, and melts at 110°. The *hydrochloride* forms yellowish tables which melt at 240°; these are monoclinic, $a : b : c = 1{\cdot}0024 : 1 : 2{\cdot}0718$; $\beta = 90° 33'$, and are twinned relatively to the basal plane. The *platinochloride* forms bundles of yellow prisms, decomposing above 300°; the *dichromate*, microscopic, reddish-yellow needles, decomposing at 100°; the *picrate*, lustrous, yellow plates melting at 220°. Nitroisoquinoline also forms *compounds* (1 mol. of each) with *methyl iodide*, as reddish-yellow prisms melting at 195°; with *ethyl bromide*, as almost colourless, lustrous needles melting at 219—220°; and with *benzyl chloride*, as faintly yellowish tables melting at 205°. Nitroisoquinoline is oxidised by permanganate to nitrophthalic acid [$(COOH)_2 : NO_2 = 2 : 3 : 1$ or $2 : 3 : 4$], and this, when heated with bromine (1 mol.) for two hours at 100° in a sealed tube, yields the bromonitroisoquinoline obtained by Edinger and Bossung (Abstr., 1891, 580) by nitrating bromisoquinoline, of which it is only known that the bromine is in the pyridine ring. By reducing nitroisoquinoline with aqueous stannous chloride, *amidoisoquinoline* is obtained; it formed yellowish needles, but was not quite pure, for it melted in one case at 128—130°,

in another at 154°. The *hydrochloride*, with 2HCl, forms colourless needles, melting with decomposition at 200°; the *platinochloride*, with $\frac{1}{2}H_2PtCl_6$, a yellowish, crystalline precipitate, turning brown at 300°; the *picrate*, a yellow precipitate, decomposing above 200°. By oxidation of a dilute aqueous solution of isoquinoline and boric acid with bleaching powder, and subsequent treatment of the product with ether, a substance was obtained in nearly white needles melting at 218°; it contained chlorine, and when dissolved in hot aqueous potash and reprecipitated with carbonic anhydride, yielded a chlorhydroxyisoquinoline, $C_9NH_5Cl{\cdot}OH$, in colourless crystals melting at 238°.

C. F. B.

Phenometadiazine Derivatives. By A. Bischler and W. Oser (*Ber.*, **26**, 1891—1903).—A new synthesis of these derivatives has been accomplished in the following manner. The oxime of an orthoacidamidocarbonyl compound is reduced at 15° in alcoholic solution with sodium amalgam, the solution being kept acid with acetic acid; the amine thus formed yields, by condensation with strong hydrochloric acid, zinc chloride, or, better, phosphorus pentoxide, a phenodihydrometadiazine.

$$C_6H_4\!<\!\begin{matrix}CR{:}NOH\\NH{\cdot}CRO\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}CHR{\cdot}NH_2\\NH{\cdot}CRO\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}CHR{\cdot}N\\NH{-}C\,R\end{matrix}.$$

Oxime. Amine. Phenodihydrometadiazine.

Orthacetamidobenzaldoxime, $NHAc{\cdot}C_6H_4{\cdot}CH{:}NOH$, obtained from orthacetamidobenzaldehyde and hydroxylamine, forms lustrous, colourless crystals melting at 194°. When reduced, it yields *orthacetamidobenzylamine*, which was obtained as an oil; its *benzoyl derivative* forms small, white, asbestos-like needles melting at 170°. The amine yields, by condensation, *pheno-2-methyldihydrometadiazine*, yellow oil with an odour of mice, boiling at 260—270°, the *hydrochloride* of which forms short, colourless prisms, the *picrate*, stellate groups of orange-yellow needles melting at 165—167°. By successive treament of the diazine with methylic iodide and potash, *pheno-2 : 3-dimethyldihydrometadiazine* is obtained; it crystallises in small, white needles, and melts at 124—126°. These two diazines are isomeric with the β-methyl- and $\beta\gamma$-dimethyl-dihydroquinazoline of Gabriel and Jansen (Abstr., 1892, 217).

α-Orthacetamidophenylethylamine, $NHAc{\cdot}C_6H_4{\cdot}CHMe{\cdot}NH_2$, is obtained as an oil by reducing the oxime of orthacetamidoacetophenone, or, better, the acetic derivative of this; when treated with benzoic anhydride, a *dibenzoyl derivative* of *orthamidophenylethylamine* is obtained in nodular aggregates of colourless needles melting at 156—157°; it was also prepared directly from *α-orthamidophenylethylamine*, obtained as an oil by reducing orthamidoacetophenonoxime. This amine also yields a *hydrochloride* in colourless prisms which soften at 187°; a *dihydrochloride* as a white, crystalline powder; a *picrate* in yellow needles melting at 160—170°; and a *diacetic derivative* as colourless, flattened needles melting at 131°. The above-mentioned α-orthacetamidophenylethylamine yields, by condensation, *pheno-2 : 4-dimethyldihydrometadiazine* as a brown

fluorescent oil, boiling at 280° under 722 mm. pressure, of which the *picrate* forms lemon-yellow crystals melting at 173°, and the *platinochloride*, orange-yellow crystals melting with decomposition at 205—206°.

When the oxime of orthacetamidoacetophenone is reduced, much of it is converted into the 1′ : 3′-acetylmethylisindazole,

$$C_6H_4<\begin{matrix}CMe\\NAc\end{matrix}>N,$$

of Auwers and v. Meyenburg (Abstr., 1892, 1376), which is, in fact, obtained directly by the action of hydroxylamine on orthacetamidoacetophenone in neutral or faintly acid solution. It crystallises with $3H_2O$, and then melts at 63°; the authors think that its constitution may perhaps be represented by $C_6H_4<\begin{matrix}CMe{:}N\\N{:}CMe\end{matrix}>O$, instead of by the above formula. C. F. B.

New Synthesis of Pyrazole Derivatives. By A. Bischler and W. Oser (*Ber.*, **26**, 1881—1890).—More pyrazole derivatives have been prepared by the method already described (this vol., i, 44). Paradiazotoluene chloride and ethylic phenacylacetoacetate yield *1-paratolyl-5-phenylpyrazole-3-carboxylic acid*, $C_7H_7\cdot N<\begin{matrix}N=C\cdot COOH\\CPh{:}CH\end{matrix}$, in crusts of lustrous, yellow prisms melting at 194—195°, together with the α-paratolylhydrazone of αβ-diketobutyric acid,

$$CMeO\cdot C(N_2H\cdot C_7H_7)\cdot COOH.$$

Orthodiazotoluene chloride yields the corresponding orthotolyl compounds, in crusts of orange-yellow prisms melting at 170—171°, and as lustrous, orange-yellow needles melting at 135° respectively, and, in addition to these, the tolueneazo-compound of the first, $C_7H_7\cdot N<\begin{matrix}N=C\cdot COOH\\CPh{:}C\cdot N_2\cdot C_7H_7\end{matrix}$, as orange-red needles melting at 179°. Diazobenzene chloride and ethylic acetonylacetoacetate yield *1-phenyl-5-methylpyrazole-3-carboxylic acid*, with $1H_2O$, in groups of flattened, colourless, lustrous needles, melting at 106° (when anhydrous at 134—135°), together with the α-phenylhydrazone of αβ-diketobutyric acid. Diazobenzene chloride and ethylic desylacetoacetate yield 1 : 4 : 5-*triphenylpyrazole-3-carboxylic acid* in stellate groups of lustrous, yellow needles melting with decomposition at 245°; this substance, when heated, loses carbonic anhydride and the residue distils at 400°; from the distillate, 1 : 4 : 5-triphenylpyrazole is obtained in nodular aggregates of small, white, silky needles melting at 212°. Diazobenzene chloride and phenacylacetic acid in alkaline solution yield a small quantity of a substance which crystallises in dark red prisms, and melts at 132°, together with a substance, probably 1 : 5-*diphenyl-3-acetylpyrazole*, which crystallises in nodular aggregates of flattened nacreous needles and melts at 88°.

C. F. B.

Pyrazolone from Ethylic Acetylenedicarboxylate. By R. v. ROTHENBURG (*Ber.*, **26**, 1719—1722).—Ethylic acetylenedicarboxylate reacts with hydrazine hydrate in absolute alcoholic solution even more readily than the oxalacetate, and yields ethylic pyrazolone-3-carboxylate, together with some pyrazolone-3-carboxylic hydrazide, and a small quantity of a substance which crystallises in white needles, and melts at 87°; it then becomes solid, and melts again at 242°. The pyrazolonecarboxylate was converted into pyrazolone by the stages already described (this vol., i, 180). C. F. B.

Pyrazolone from Ethylic Propiolate. By R. v. ROTHENBURG (*Ber.*, **26**, 1722—1724).—When ethylic propiolate in absolute alcoholic solution is treated with hydrazine hydrate, pyrazolone is formed to the extent of 25—30 per cent. of the theoretical yield, but it cannot readily be isolated. From the acid solution were prepared various salts, of which the *silver salt* has the composition $C_3H_4N_2O,C_3H_3AgN_2O$. An aqueous solution treated successively with sodium nitrite and silver nitrate gives a *silver salt*, $\begin{matrix}N{=}CH\\ |\\ NH{\cdot}CO\end{matrix}\!\!>\!C{:}NOAg$. A feebly alkaline solution, treated with paradiazotoluene sulphate, yields *pyrazolone-4-parazotoluene*, $\begin{matrix}N{=}CH\\ |\\ NH{\cdot}CO\end{matrix}\!\!>\!C{:}N{\cdot}NH{\cdot}C_6H_4Me$, which crystallises in tiny, reddish-purple plates, melting at 219°. C. F. B.

Phenylpyrazolidine. By A. MICHAELIS and O. LAMPE (*Annalen*, **274**, 316—331; compare Abstr., 1892, 355).—Phenylpyrazolidine (*loc. cit.*) has a sp. gr. of 1·20 at 15°, does not solidify when cooled to −15°, and gives an intense red coloration when dissolved in dilute hydrochloric acid and treated with potassium dichromate. The *hydrochloride* is a white crystalline powder, and melts at 167—168° with decomposition; a platinochloride, or aurochloride could not be obtained on account of the reducing property of the substance. The *hydrobromide* melts at 147°; the *hydriodide* at 131—132° with decomposition; and the *picrate* at 102° with decomposition. The *acetyl* derivative, $C_9H_{11}N_2Ac$, is an odourless, fluorescent oil which boils at 231—232° (110 mm.); and the *benzoyl* derivative, $C_9H_{11}N_2Bz$, melts at 79°. Both of the last-described compounds give red colorations with potassium dichromate and hydrochloric acid.

Benzylidenephenylpyrazolidine, $NH\!<\!\begin{matrix}NPh{\cdot}CH_2\\ |\\ CH_2{\cdot}C{:}CHPh\end{matrix}$, obtained by heating phenylpyrazolidine with benzaldehyde at 150° in an atmosphere of carbonic anhydride, is an oil boiling at 280—290° (100 mm.).

Diphenylpyrazolidinesemicarbazide, $NHPh{\cdot}CO{\cdot}N\!<\!\begin{matrix}NPh{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}$, is formed, with evolution of heat, when phenylpyrazolidine is treated with phenylcarbimide; it forms silky leaflets, and melts at 114°.

Diphenylpyrazolidinethiosemicarbazide, $NHPh{\cdot}CS{\cdot}N\!<\!\begin{matrix}NPh{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}$, is prepared from phenylthiocarbimide and phenylpyrazolidine; it forms lustrous needles, and melts at 164—165°.

Phenylmethylpyrazolidine, $NPh<^{CH_2\cdot CH_2}_{NMe\cdot CH_2}$, obtained by treating phenylpyrazolidine with methylic iodide and alcoholic alkali, is a yellow oil which boils at 175—180° (90 mm.): it gives an intense red coloration in dilute solution with potassium dichromate and hydrochloric acid. *Phenylbenzylpyrazolidine*, $CH_2Ph\cdot N<^{NPh\cdot CH_2}_{CH_2\cdot CH_2}$, prepared from phenylpyrazolidine, benzyl chloride, and alcoholic alkali is a yellowish oil, boils at 225° (40 mm.), and gives in dilute solution with potassium dichromate and hydrochloric acid, a permanent blue coloration. A. R. L.

Pyrazines. By C. Stoehr (*J. pr. Chem.* [2], **48**, 18—23; compare this vol., i, 486).—The author notices the chief points of difference between his previous paper and that of Wolff (this vol., i, 373) on this subject; to these attention has already been called (this vol., i, 486). To convince himself that Wolff's base is identical with his own, the author has prepared the salts described by Wolff from his own sample of the base; the results were practically identical with those obtained by Wolff. The paper concludes with a brief consideration of the probable manner in which the bonds in the pyrazine ring are disposed. A. G. B.

Synthesis of Pyrazine. By L. Wolff (*Ber.*, **26**, 1830—1833); compare Abstr., 1888, 809).—The gold salt previously obtained by the author from the products formed by heating acetalamine with oxalic acid (Abstr., 1888, 809) has now been proved to be a salt of pyrazine and to have the formula $C_4H_4N_2,AuCl_3$. A yield of about 20 per cent. of the theoretical amount of the base may be obtained from acetalamine by adding 1 part of the latter to a concentrated warm solution of 3 parts of mercuric chloride, and then sufficient concentrated hydrochloric acid to dissolve the double salt which is precipitated. The liquid is then boiled for 10 minutes, filtered, rendered alkaline with anhydrous sodium carbonate, and distilled with steam. The distillate is acidified with hydrochloric acid, distilled to remove alcohol, &c., and the pyrazine then converted into the double salt with mercuric chloride, which is finally distilled with a very concentrated solution of potassium carbonate. The pure base is thus obtained as an oil which soon solidifies to white needles. A. H.

Methyldipyridyls. By B. C. Stoehr and M Wagner (*J. pr. Chem.*, [2] **48**, 1—16; compare Abstr., 1891, 80; 1892, 75).—$\beta\beta$-Dimethyldipyridyl is prepared from β-methylpyridine by a method similar to that employed for making the $\alpha\alpha$-derivative from α-methylpyridine (Abstr., 1891, 80). The portion which distils at 280—290° crystallises, and is washed by ether free from alcohol. It is sparingly soluble in water and only slightly volatile with steam. It crystallises in small, lustrous tables or prisms, melts at 125°, and boils at 293° at the ordinary pressure, almost without decomposition. It is precipitated from its aqueous solution by alkalis, and is heavier

than water. Potassium ferrocyanide does not precipitate its solutions, but an orange-red ferrocyanide gradually separates when this reagent is added to them. It behaves as a diacid base. The *hydrochloride*, $C_{12}H_{12}N_2,2HCl$, crystallises in slender, lustrous needles; it sublimes without melting. The *platinochloride*, $C_{12}H_{12}N_2,H_2PtCl_6$, crystallises in flat, reddish-yellow needles, or serrated laminæ. The *platinum* salt, $C_{12}H_{12}N_2,PtCl_4$, the *mercurochloride*,

$$C_{12}H_{12}N_2,2HCl,4HgCl_2$$

(m. p. 221—222°), the *aurochloride*, $C_{12}H_{12}N_2,2HAuCl_4$, the *argentonitrate*, the *picrate*, $C_{12}H_{12}N_2,2C_6H_3N_3O_7$, the *methiodide*, $C_{12}H_{12}N_2,2MeI$, with its *cadmioiodide*, $C_{12}H_{12}N_2,2MeI,CdI_2$, and the *methochloride*, $C_{12}H_{12}N_2,2MeCl$, with its *platinochloride*, $C_{12}H_{12}N_2,2MeCl,PtCl_4$, and its *mercurochloride*, $C_{12}H_{12}N_2,2MeCl,4HgCl_2$ (m.p. 148—149°) are described.

Dipyridyl-ββ-dicarboxylic acid, $C_{10}H_6N_2(COOH)_2$, is the product of the oxidation of *ββ*-dimethyldipyridyl by potassium permanganate at the temperature of the water-bath; it crystallises in small, lustrous prisms (with 2 mols. H_2O), and is more soluble in water than is the *αα*-acid (Abstr., 1892, 75) but dissolves very sparingly in ether, alcohol, chloroform, and benzene. It is not coloured by ferrous sulphate, and may be heated at 280° without apparent change. The *ammonium* salt is very soluble in water, the *calcium* salt crystallises well, the *copper*, *silver*, *lead*, *mercury*, *cobalt*, and *nickel* salts are more or less insoluble, amorphous precipitates.

When the acid is heated with glacial acetic acid at 300°, the carboxyl groups are eliminated and a salt of *γγ*-dipyridyl is obtained. This proves the dimethylderivative to be a *γγ*-dipyridyl compound.

ββ-Dimethyl-γγ-dipiperidyl, $C_{12}H_{24}N_2$, is prepared by acting on *ββ*-dimethyl-*γγ*-dipyridyl with nascent hydrogen from sodium and water, and is purified by taking advantage of the insolubility of its hydrochloride in alcohol. It is a colourless, viscid oil, boils at 299—300° (corr.), and gradually crystallises; it is unusually soluble in water, with an alkaline reation, and is also soluble in alcohol and ether; it has a bitter taste and a narcotic odour. The *hydrochloride*, $C_{12}H_{24}N_2,2HCl$, crystallises in dazzling white needles, and is unchanged at 290°. The *platinochloride*, $C_{12}H_{24}N_2,H_2PtCl_6 + 2\frac{1}{2}H_2O$, crystallises in reddish-yellow laminæ, darkens at 250°, and melts at 256—258°. The *mercurochloride*, $C_{12}H_{24}N_2,2HCl,4HgCl_2$ (m. p. 210—211°), the *cadmioiodide*, $C_{12}N_{24}H_2,2HI,CdI_2$ (m. p. 270—272°), and the *nitrosamine* are described. A. G. B.

Relation of Safranines to Indulines. By O. Fischer and E. Hepp (*Ber.*, **26**, 1655—1657; see also *Ber.*, **26**, 1194).—When phenosafranine is diazotised in alcoholic solution in the presence of hydrochloric acid, the hydrochloride of a compound which the authors name *aposafranine* is obtained. If the salt is heated with $2\frac{1}{2}$ times its weight of aniline in the water bath, until the product dissolves in concentrated sulphuric acid with a reddish-violet coloration, it is converted into the hydrochloride of the induline, $C_{18}H_{13}N_3$. The latter crystallises in beautiful, lustrous, green prisms,

and gives a reddish-violet solution with concentrated and dilute mineral acids. When heated with dilute sulphuric acid under pressure, it yields benzolindone hydrate (*Annalen*, **266**, 253). It is, therefore, the simplest induline, $NH{:}C_6H_3{<}\overset{N}{\underset{NPh}{}}{>}C_6H_4$. When heated with aniline at 140—150°, it is converted into phenylinduline (m. p. 231°), which is identical with the compound obtained from azophenine, and with that obtained from the amidophenylinduline of the amidobenzene melt. Hence the authors conclude that in the preparation of induline from amidoazobenzene, a safranine is formed as an intermediate compound. E. C. R.

Alkaloïds of Gelsemium sempervirens. By A. R. Cushny (*Ber.*, **26**, 1725—1727).—The following two have been isolated:—

Gelsemine [Eng. "Gelsemin (Gerrard)"; Ger. "Krystallisirtes Gelseminin"] is white, amorphous, bitter, and strongly alkaline; its salts are crystalline. Sulphuric acid and manganese dioxide or potassium dichromate give a red coloration, changing gradually to green. In the frog it causes tetanic convulsions, and finally deadening of the sensory nerve-endings; on rabbits it has no effect. The *hydrochloride* is $C_{19}H_{23}N_3O_{14},2HCl$.

Gelseminine (Ger. "Gelseminin amorph.") is colourless, amorphous, strongly alkaline; the salts are amorphous. Sulphuric acid and oxidising agents give a violet coloration, changing to green. It is very poisonous, producing respiratory failure in rabbits as well as in frogs; it also causes dilatation of the pupil. The *platinochloride* is stated to have the formula $C_{42}H_{47}N_3O_{14},HCl,PtCl_4$ (!). C. F. B.

Ptomaïne from the Urine in Cases of Eczema. By A. B. Griffiths (*Compt. rend.*, **116**, 1205—1206).—The urine of patients suffering from eczema yields a ptomaïne, $C_7H_{15}NO$, which is not obtained from normal urine. It is a white, crystalline compound, soluble in water, and having a feebly alkaline reaction. It yields a crystalline hydrochloride, aurochloride, and platinochloride. With phosphotungstic acid, its solutions yield a brownish precipitate; with phosphomolybdic acid, a yellowish precipitate; with picric acid, a yellow precipitate; with silver nitrate, a yellowish precipitate; with mercuric chloride, a greenish precipitate, and a precipitate also with Nessler's reagent.

The base is poisonous, and when injected under the skin of a rabbit produces local inflammation with high fever, resulting in death. C. H. B.

Chitins. By N. P. Krawkow (*Zeit. Biol.*, **29**, 177—198).—From the examination of the chitinous skeleton of various invertebrates, the following conclusions are drawn:—

1. There are various kinds of chitin, differing from one another in the reaction they give with iodine.

2. Chitins are amido-derivatives of carbohydrates.

3. The carbohydrate derivatives give reactions with iodine very similar to those of the chitins from which they are obtained.

4. The different kinds of chitins may assist in the zoological classification of the animals which yield them.

5. Chitin resembles the pathological substance amyloïd in its behaviour to iodine and aniline dyes.

6. The occurrence of cellulose in animals is only proved in the case of the Tunicates. In Arthropods and Cephalopods its presence appears to be in the highest degree doubtful.

7. In chitinous tissues, chitin is in loose chemical combination with proteïd material. W. D. H.

δ-Achroglobulin from the Blood of certain Mollusca. By A. B. Griffiths (*Compt. rend.*, **116**, 1206—1207).—δ-Achroglobulin is obtained from the blood of certain species of *Doris*, and exists in a reduced and in an oxidised condition. It has the composition $C_{639}H_{792}N_{165}SO_{153}$, and 100 grams absorb 125 c.c. of oxygen at normal temperature and pressure. A solution in a dilute magnesium sulphate solution has the specific rotatory power $[\alpha]_D = -54°$.

δ-Achroglobulin yields with methane a yellowish compound, with acetylene a greenish compound, and with ethylene a brownish compound, and each of them dissociates in a vacuum. C. H. B.

Proteïd Reactions. By J. W. Pickering (*J. physiol.*, **14**, 347—382).—Cobalt salts and potash give distinctive colour reactions with proteïds, proteoses, and peptones. Native proteïds give a heliotrope purple; proteoses and peptone a red-brown. Certain albuminoïds (gelatin, mucin, keratin elastin, &c.) and various organic substances related to proteïds (biuret, alloxan, uric acid xanthine, hypoxanthine, &c.), give similar colours.

Gelatin gives a play of colours in spectral order; so also do alloxan, biuret, and allantoïn.

It is regarded as probable that these reactions, like those similarly produced with copper salts (the so-called biuret reaction) and nickel salts (Gnezda), are due to the presence of the group CONH, and not to cyanogen, as Gnezda considered; the difference between a native proteïd and a peptone being one in the atomic arrangement of the group.

When a cobalt salt has entered into the proteïd molecule, it can be easily displaced by a nickel salt, and that in turn by a copper salt, each in turn yielding its characteristic colour reaction.

The precipitates of proteïd produced by mercuric chloride, silver nitrate, salicylsulphonic, phosphotungstic, and phosphomolybdic acids yield typical proteïd colour reactions. The nucleo-albumins behave as ordinary proteïds, not as peptones, in their colour reactions.

The xanthoproteïc reaction and Millon's reaction probably are due to a hydroxybenzene nucleus in the proteïd molecule. The reactions of Liebermann and Adamkiewicz depend on the aromatic portion of the proteïd molecule. Krasser's reaction (a brilliant red with solution of alloxan) probably depends on an amido-group, as stated by Krasser himself.

When metamidobenzoic acid is heated with phosphorus pentachloride, it yields a substance which behaves as Grimaux stated, very

like a proteïd, coagulating with heat, especially in presence of a calcium salt. The evidence that Grimaux advanced that this "colloide amidobenzoique" is free from calcium phosphate is not regarded as satisfactory. It is, however, to be noted that this material gives, with alkaline solutions of copper, nickel, and cobalt, reactions like those of a proteïd.

No evidence was found that Fröhde's reaction (blue precipitate when a solid proteïd is heated with sulphuric and molybdic acids) and Axenfeld's reaction (blue appearance when a proteïd is heated with auric chloride and formic acid, gas being given off) are due to any special molecular group. In connection with the last-named reaction, it was found that if the heating is continued for five minutes at the boiling point, the auric chloride is reduced, and a mirror of gold lines the test-tube. W. D. H.

Hæmoglobin which contains Phosphorus. By Y. Inoko (*Zeit. physiol. Chem.*, **18**, 57—60).—Hoppe-Seyler and, later, Jaquet showed that the blood crystals from birds contain phosphorus. This has been explained by the existence of a nucleus in their blood corpuscles. The present investigation relates to (1) whether nucleïc acid can be obtained from birds' blood crystals, and (2) whether an analogous crystalline compound can be obtained by adding nucleïc acid to the oxyhæmoglobin of mammals' blood. The answer to the first question is almost certainly in the affirmative, as adenine was prepared from the crystals. With regard to the second point, oxyhæmoglobin from horses' blood was dissolved in a solution of nucleïc acid, and cooled to 0°, when a substance crystallised out in prisms which contained 0·4 per cent. of phosphorus, that is, approximately the same as in the blood crystals of the goose. W. D. H.

Dissociation of Oxyhæmoglobin in Aqueous Solution. By G. Hüfner (*Zeit. physikal. Chem.*, **11**, 794—804).—The author shows that for solutions of oxyhæmoglobin varying in concentration from 10 to 17·5 grams per litre, the extinction-coefficient is proportional to the concentration, and attributes the discrepancy between his results and those of van Noorden (*Zeit. physiol. Chem.*, **4**, 23) to the different photometric methods employed. There is, therefore, probably no decomposition of large molecular aggregates into smaller as the dilution increases. There is, however, in all solutions a dissociation of oxyhæmoglobin into free oxygen and hæmoglobin. The author endeavoured to show this by a change of colour in a solution of hæmoglobin, separated from a solution of oxyhæmoglobin by a membrane of vegetable parchment, which allows oxygen and water to pass through it, but is impermeable to the other substances. No definite result was obtained, probably owing to the destruction of the oxygen by a reducing substance before it could pass through the membrane. J. W.

Organic Chemistry.

Formation of Hydrocyanic acid by the Action of Nitric acid on Sugar, &c. By F. B. Burls, R. E. Evans, and C. H. Desch (*Chem. News*, **68**, 75).—The authors find that hydrocyanic acid is formed during the action of nitric or nitrous acid on sugar, caramel, or finely divided charcoal. D. A. L.

Pentaglycerol. By H. Hosaeus (*Annalen*, **276**, 75—79).—Pentaglycerol, $CMe(CH_2\cdot OH)_3$, is obtained by the action of formaldehyde (3 mols.) on propaldehyde (1 mol.) in presence of water and calcium hydroxide; it crystallises from alcohol in white needles, melts at 199°, sublimes without decomposition, and is very easily soluble in water. The *triacetyl* derivative, $C_5H_9(OAc)_3$, is a colourless liquid, and the *tribenzoyl* derivative, $C_5H_9(OBz)_3$, forms colourless needles. When pentaglycerol is heated in a reflux apparatus with potassium dichromate and sulphuric acid, formic and acetic acids are produced. A. R. L.

Penterythritol. By P. Rave and B. Tollens (*Annalen*, **276**, 58—69).—Among the bye-products obtained in the preparation of penterythritol, $C(CH_2\cdot OH)_4$ (Abstr., 1892, 128), a compound has been isolated which is more soluble in water than penterythritol, and melts at 174—190°; it gave values on analysis indicating that it may be a "*tetraglycerol*," $CH(CH_2\cdot OH)_3$. The volatile bye-products consist of an aldehyde, recognised by the magenta sulphurous acid reaction, together with formic and acetic acids.

Tetrabenzoylpenterythritol, $C_5H_8(OBz)_4$, prepared by the Baumann-Schotten method crystallises in long needles, and melts at 99—101°. When penterythritol is heated for four hours at 100° with phosphorus tribromide (8 parts) and subsequently at 150°, the product extracted with cold alcohol, and the residue boiled with alcohol and filtered from phosphorus, the *tetrabromhydrin*, $C_5H_8Br_4$, separates from the filtrate in colourless leaflets; it melts at 154—156°. The *tribromhydrin*, $C_5H_8Br_3\cdot OH$, is obtained from the cold alcoholic extract; it is also produced by heating penterythritol with phosphorus tribromide at a temperature not higher than 100°; it melts at 60°.

When penterythritol is oxidised with nitric acid of 1·4 sp. gr., oxalic and glycollic acids are obtained, but if dilute nitric acid in the cold is employed, *diglycollaldehyde*, $CHO\cdot CH_2\cdot O\cdot CH_2\cdot CHO$, is obtained. The latter forms a *hydrazone*, $C_{16}H_{18}N_4O$, melting at 108°.

When penterythritol tribromhydrin is treated with zinc dust and acetic acid, an unsaturated alcohol, $C_5H_9\cdot OH$, is obtained, boiling at 120—128°; it does not solidify when cooled to −30°. A similar compound is formed by acting with zinc dust and acetic acid on penterythritol triiodhydrin. A. R. L.

Carbohydrates of the Jerusalem Artichoke. By C. Tanret (*Compt. rend.*, **117**, 50—53).—The juice of Jerusalem artichokes, after

treatment with basic lead acetate and removal of the lead, is mixed with barium hydroxide and fractionally precipitated with alcohol, the process of fractionation being repeated on the products.

Two carbohydrates, much more soluble in alcohol than inulin, pseudoinulin, or inulenin, are thus obtained.

Helianthenin crystallises in microscopic needles which melt at 176°. When dried at 110°, it has the composition $12C_6H_{10}O_5 + 3H_2O$. It is soluble in its own weight of water, and is also very soluble in dilute alcohol, but the solubility diminishes rapidly as the concentration of the alcohol increases. Its rotatory power is $[\alpha]_D = -23{\cdot}5°$, but under the influence of dilute acids this increases to $-70{\cdot}2°$. Helianthenin is fermented by beer yeast with some difficulty under ordinary conditions.

Synanthrin, which when dried at 110° has the composition $8C_6H_{10}O_5 + H_2O$, is amorphous and almost tasteless. It melts at 170°, dissolves in all proportions in water or dilute alcohol, and in 10 parts of alcohol of 84°. Its rotatory power is $[\alpha]_D = -17°$, and when treated with dilute acids this rises to $-70{\cdot}6°$ owing to the formation of glucose and levulose. Synanthrin is fermentable. It has the peculiar property of preventing the formation of barium saccharate, which only forms when at least 1·5 parts of saccharose is present for 1 part of synanthrin. The inactive sugar said to be obtained from artichokes and described as levulin or synanthrose is a mixture of saccharose and synanthrin.

Helianthenin and synanthrin also occur in the dahlia and in elecampane. C. H. B.

Lime Tree Honey. By MAQUENNE (*Compt. rend.*, **117**, 127—129). The fresh leaves of the lime tree, when treated simply with water and evaporated on a water bath to a syrupy consistence, yield about 1 per cent. of a very sweet, brown syrup with a bitter after-taste. If this is treated with alcohol of 90°, a gummy substance is precipitated, and the liquid deposits microscopic crystals which do not consist of saccharose. After purification by repeated crystallisation from alcohol, the crystals are identical with the melezitose obtained from Persian manna. Its rotatory power is $+88{\cdot}8°$, and is reduced to about 50° after complete hydrolysis; when boiled with phenylhydrazine acetate, it yields ordinary well crystallised phenylglucosazone and gelatinous *phenylturanosazone*, which is characteristic of the biose formed in the feeble hydrolysis of melezitose; it melts at the same temperature as melezitose from manna, and its solutions crystallise when a fragment of melezitose is introduced, but are not affected by other sugars.

The leaves contain a reducing sugar which seems to be ordinary glucose, and also a gummy substance. Approximately, 40 per cent. of the crude "lime tree honey" is melezitose. C. H. B.

Preparation of Glycogen from the Liver and Muscles. By V. KISTYAKOFFSKY (*J. Russ. Chem. Soc.*, **25**, 60—73).—Liver and muscle are taken from the animal immediately after death, and, to prevent fermentation, rubbed up at once in an iron mortar cooled to

a very low temperature. The homogeneous mass is then extracted with a cooled 1—2 per cent. solution of hydrochloric acid until the last extracts cease to give the glycogen reaction with iodine. When it is not desired to effect a complete extraction of the glycogen, acid of 0·2 to 0·7 per cent. strength may be used. The solution thus obtained is coloured by hæmoglobin, and contains albuminous matter, which is precipitated by means of mercuric iodide; this precipitate is filtered off and washed on the filter with dilute mercuric iodide solution until it is free from glycogen. The glycogen is precipitated from the filtrate and washings by the addition of alcohol (about 1·5 volumes), collected on a filter, and washed, first with 75 per cent. alcohol, and then with 95 per cent. alcohol and ether. When dried over sulphuric acid, the glycogen forms a light, amorphous, snow-white powder, containing no nitrogenous admixture, and leaving only traces of ash. Dried in the air, the glycogen is obtained in the form of a resinous mass difficult to powder. This method of cold extraction may be employed for the quantitative estimation of glycogen in animal tissues, the results obtained being somewhat lower than those arrived at by Brücke's method. J. W.

Specific Rotatory Power of Glycogen. By HUPPERT (*Zeit. physiol. Chem.*, **18**, 137—143).—The specific rotatory power of glycogen is variously given by different observers. In the present investigation, the following formula was used,

$$[\alpha]_D = \frac{\alpha}{\alpha'}\frac{12}{11}\,52{\cdot}5^\circ,$$

α being the rotation observed in the glycogen solution, α' that in the dextrose solution formed by hydrolysis from it, the tubes being of the same length. 52·5 is the specific rotatory power of dextrose, and the ratio 12 : 11 is obtained by taking the formula of glycogen as $6C_6H_{10}O_5 + H_2O$, so that 11 parts of glycogen yield 12 of dextrose. The average of five experiments gave $[\alpha]_D = +196{\cdot}63^\circ$ as the specific rotatory power of glycogen. Erythrodextrin gives the same colour with iodine as glycogen, and the spectroscopic appearances are identical. The specific rotatory power of erythrodextrin, estimated in the same way, is $+196{\cdot}5^\circ$, so that the polarimeter is of no use in distinguishing between the two substances. W. D. H.

Cryoscopy, &c., of Caramel. By A. SABANÉEFF and I. ANTUSHEVICH (*J. Russ. Chem. Soc.*, **25**, 23—31).—Dialysed caramel, prepared by repeated precipitation from its aqueous solution by alcohol, is not a carbohydrate, carbonic anhydride being given off on its formation from sugar. From determinations of its molecular weight (nearly 3000) in aqueous solution, and combustions of the substance itself, as well as analysis of the barium derivative, the author proposes the approximate formula $C_{125}H_{188}O_{80}$. The formation from sugar would then be represented by the equation

$$11C_{12}H_{22}O_{11} = C_{125}H_{188}O_{80} + 7CO_2 + 27H_2O.$$

The aqueous solution of dialysed caramel is affected by heat and by

the action of light, the depression of the freezing point increasing, probably in consequence of a process of hydration, and formation of substances with lower molecular weight. Caramel in aqueous solution is capable of undergoing a species of fermentation, in virtue of which the depression is diminished. This is a process of dehydration with formation of products of much greater molecular weight.

Gélis' caramel is dialysed caramel whose solutions have undergone change by heating, whilst Graham's mucilaginous caramel, which diffused more slowly than albumen, is the product of the specific fermentation mentioned above. J. W.

Decomposition of Ethers by Hydrogen Haloïds. By W. Lippert (*Annalen*, **276**, 148—199).—These experiments were made in order to determine the extent to which the decomposition by hydrogen haloïds of compounds consisting of two or more organic radicles and oxygen is affected by the constitution of the compounds and the constitution of their radicles.

The ethers (5—10 grams) were introduced into tubes sealed at one end, and saturated at 0° with the hydrogen haloïd; the open ends of the tubes were then sealed, and they were heated at 100°.

The ethers were prepared by Williamson's method, namely, acting on the alkyl haloïds with the sodium or potassium alkyloxides; the alkyloxides prepared from the secondary and also from the higher primary alcohols must be free from an excess of the alcohol. The dissolution of sodium in the primary alcohols takes place more readily than in the secondary and tertiary alcohols. Attempts to combine trimethylcarbinylic iodide with pyridine were unsuccessful, although the isomeric butylic iodides combine with it readily to form crystalline compounds.

The vapour densities of the dialkylethylene ethers were determined in a Gay Lussac-Hofmann apparatus as modified by Lothar Meyer, so that the vapour tensions could be determined with one and the same quantity of substance at different temperatures, and under pressures varying from a few millimetres of mercury up to 2 atmospheres. The vapour tensions observed between 10° and 100° are represented by curves, from an inspection of which it is evident that the vapour tensions of the dialkylethylene ethers vary inversely as the number of carbon atoms in their molecules.

The general results are in harmony with Silva's rule in the following modified form. When a mixed ether is decomposed by a hydrogen haloid, the halogen combines with the radicle of lower equivalent. In the case of bi- and ter-valent ethers, the halogen generally combines with the univalent radicles. The smaller the number of carbon atoms contained in its radicles, the easier the decomposition of an ether.

When hydrogen iodide acts on a mixed ether containing isomeric radicles, the halogen combines with the normal hydrocarbon radicle. When both radicles are derived from the same hydrocarbon, the halogen combines with that of primary structure. Propyl isopropyl ether forms an exception to this rule, as in this case the halogen combines with the isopropyl group.

The action of hydrogen iodide is in all cases more energetic than that of hydrogen bromide.

The results are tabulated below.

a. Univalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$CHMe_2 \cdot O \cdot Et$	EtI	$CHMe_2 \cdot OH$
$CH_2 \cdot CHMe_2 \cdot O \cdot Et$	EtI	$CHMe_2 \cdot CH_2 \cdot OH$
$CH_2 \cdot CH \cdot CH_2 \cdot O \cdot Pr^n$	$CH_2 \cdot CH \cdot CH_2I$	$Pr^n \cdot OH$
$CH_2 \cdot CH \cdot CH_2 \cdot O \cdot CHMe_2$	$CH_2 \cdot CH \cdot CH_2I$	$CHMe_2 \cdot OH$

b. Univalent Ethers with Isomeric Radicles.

Ethers.	Haloïds.	Hydroxides.
$CHMe_2 \cdot O \cdot Pr^n$	$CHMe_2I$	$Pr^n \cdot OH$
$CH_2Me \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CHMe_2$	$CH_2Me \cdot CH_2 \cdot CH_2I$	$CHMe_2 \cdot CH_2 \cdot OH$
$CH_2Me \cdot CH_2 \cdot CH_2 \cdot O \cdot CHMeEt$	$CH_2Me \cdot CH_2 \cdot CH_2I$	$CHMeEt \cdot OH$
$CHMeEt \cdot O \cdot CH_2 \cdot CHMe_2$	$CHMeEtI$	$CHMe_2 \cdot CH_2 \cdot OH$

c. Bivalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$CH_2(OMe)_2$	2MeI	HCOH
$CH_2(OEt)_2$	2EtI	HCOH
$CH_2(OPr^n)_2$	$2Pr^nI$	HCOH
$CH_2(OC_5H_{11})_2$	$2C_5H_{11}I$	HCOH
$CHMe(OEt)_2$	2EtI	MeCOH
$C_2H_4(OMe)_2$	2MeI	$C_2H_4(OH)_2$
$C_2H_4(OEt)_2$	2EtI	$C_2H_4(OH)_2$
$C_2H_4(OPr^n)_2$	$2Pr^nI$	$C_2H_4(OH)_2$
$C_2H_4(OC_4H_9)_2$	$2C_4H_9I$	$C_2H_4(OH)_2$

d. Tervalent Ethers.

Ethers.	Haloïds.	Hydroxides.
$CH(OEt)_3$	3EtI	HCOOH
$CH(OPr^n)_3$	$3Pr^nI$	HCOOH
$C_3H_5(OEt)_3$	3EtI	$C_3H_5(OH)_3$

A. R. L.

Zinc Isopropide. By V. Ragozin (*J. Russ. Chem. Soc.*, **24**, 549—552).—Isopropylic iodide (170 grams), mixed with absolute ether (100 grams), is heated to boiling on the water bath with granulated zinc (100 grams) and powdered zinc sodium (2—3 grams). The reaction is complete in nine hours, and the contents of the flask are then distilled in a current of dry carbonic anhydride, first from the water bath and afterwards from an oil bath. The higher boiling portion, on redistillation, gives a fraction boiling at 135—137°, which consists of nearly pure zinc isopropide. The yield is about 20 per cent. of that theoretically possible.

Zinc isopropide cannot be prepared in the pure state, as it decomposes more or less on distillation, even under reduced pressure. Under a pressure of 40 mm. it boils between 94° and 98°. It is a clear, colourless liquid, which fumes strongly in the air, but may be transferred from one vessel to another without igniting. When spread over a large surface, however, it inflames spontaneously. Exposed to the slow action of air in a closed vessel, it absorbs oxygen with formation of zinc isopropoxide, $Zn(OPr^{\alpha})_2$, which separates in prismatic crystals. J. W.

Alkyl Compounds of Magnesium. By H. Fleck (*Annalen*, **276**, 129—147).—A continuation of Löhr's experiments (Abstr., 1891, 682). Magnesium amalgam acts on ethylic iodide with development of heat when the two are brought together in an exhausted sealed tube, but to complete the reaction it is necessary to heat the tubes at 100°, magnesium diethide and gaseous products being formed. Aluminium amalgam has no action on ethylic iodide at the ordinary temperature, but when the two are heated at 130°, gaseous products, and much mercuric and aluminium iodides are obtained, together with a liquid containing aluminium. An alloy of zinc and magnesium acts on ethylic iodide at 120°, forming a little magnesium diethide and a large amount of metallic iodides. Magnesium-cadmium alloy acts on ethylic iodide at 120°, forming normal butane and other hydrocarbons, together with metallic iodides. Magnesium diethide, prepared by Löhr's method, reacts with water, forming ethane and magnesium iodide.

Trimethylcarbinol is obtained by the action of acetic chloride on magnesium dimethide, and the same compound is formed from acetic chloride and magnesium diethide, but certain hydrocarbons are simultaneously produced.

Magnesium diphenyl is prepared by heating mercury diphenyl with an excess of magnesium powder in an exhausted sealed tube at 200—210° for 5—6 hours. The tube is opened under benzene, heated on the water bath with some of this solvent, which dissolves the excess of mercury diphenyl, after which the magnesium diphenyl is extracted with a mixture of ether and benzene, and the solution evaporated in an atmosphere of dry nitrogen; it is a light grey substance, insoluble in carbon bisulphide, ether, and benzene, although it dissolves freely in a mixture of the last two. With water, it gives magnesium hydroxide and benzene. It burns in air, forming magnesium oxide and a carbonaceous mass, but when a

current of dry air is passed into anhydrous benzene containing magnesium diphenyl in suspension, slow oxidation takes place, and at the end of three months the compound is converted into magnesium diphenoxide, $Mg(OPh)_2$. When bromine is slowly dropped on to magnesium diphenyl covered with a layer of anhydrous ether, it yields magnesium bromide and bromobenzene. If magnesium diphenyl is heated above 210° in a sealed tube, a tar-like mass is formed from which diphenyl may be isolated. Benzal chloride reacts with magnesium diphenyl, forming triphenylmethane, whilst phosphorus trichloride gives rise to diphenyl phosphorus chloride, $PClPh_2$ (Michaelis, 1875).

It is interesting to note that compounds such as magnesium alkyl iodides do not seem to exist; in the case of zinc and mercury these are the initial products of the action of the metals on the alkyl iodides, and they subsequently decompose, yielding metallic alkyls and iodides. The magnesium compounds are more active than the analogous zinc compounds. A. R. L.

Action of Acetylacetone on Bromacetone in presence of Sodium Ethoxide. By G. Magnanini (*Gazzetta*, **23**, i, 462—469).—Bromacetone is added to an alcoholic solution of sodium ethoxide and acetylacetone, the reaction completed by heating on the water-bath, and the product distilled in a current of steam; the residue is a heavy, red oil, which could not be purified, and decomposes on distillation. It seems to be *unsymmetrical triacetylethane*, $CHAc_2{\cdot}CH_2Ac$, and by heating either it, or the products obtained by its direct distillation, with ammonia in a sealed tube at 180°, 2 : 5-*dimethyl*-3-*acetylpyrroline*, $\begin{matrix}CAc{:}CMe\\ |\\ CH{:}CMe\end{matrix}>NH$, is obtained. This compound is identical with the substance of the composition, $C_8H_{11}NO$, obtained by Magnanini and Scheidt (Abstr., 1892, 1429) by heating dehydrodiacetyllevulinic acid with ammonia; it is a feeble base, melts at 94°, and gives a *hydrochloride*, $C_8H_{11}NO,HCl$, which is decomposed by water, and forms whitish needles which decompose at above 150°. The constitution of the base is established by the fact that it gives 2 : 5-dimethyl-3-cinnamalpyrroline when boiled with benzaldehyde and potash.

Dehydrodiacetyllevulinic acid is, therefore, a derivative of 2 : 5-dimethyl-3-acetylfurfuraldehyde, and probably has the following constitution, $O<\begin{matrix}CMe{:}C{\cdot}COOH\\ |\\ CMe{:}CAc\end{matrix}$. W. J. P.

Flowers of Tagetes glandulifera. By O. Hesse (*Annalen*, **276**, 87—88).—*Tagetes glandulifera* is a plant of the order Compositæ, met with in Argentina, where the flowers are used as a stomachic, aperient, diuretic, and diaphoretic, and are employed in cases of gastritis and indigestion. Their application is, however, said to be attended with danger.

The author finds that the flowers do not contain any alkaloïd which can be extracted with ether or chloroform. Light petroleum, however, extracts a substance which, when crystallised from alcohol,

melts at 62°; it may be cerylic acetate, as the alcohol obtained on hydrolysis agreed in properties with cerylic alcohol, and the original substance was regenerated by treating the alcohol with acetic anhydride; no analyses or other data are given. A. R. L.

Thermochemistry of Chloracetic acid. By S. Tanatar (*J. Russ. Chem. Soc.*, **24**, 694—698).—The unstable modification of chloracetic acid (m. p. 52°) changes into the stable modification (m. p. 63°) with development of heat = 0·65 Cal. per gram-molecule. The heat of dissolution of the stable acid was found to be −3·47 Cal., and that of the unstable acid −2·77 Cal., giving a difference of 0·70 Cal., nearly equal to the heat of transformation directly observed. Both acids show a normal molecule in aqueous solution, and a double molecule in benzene solution. J. W.

Decomposition of Chloracetates and Bromacetates. By J. H. Kastle and B. C. Keiser (*Amer. Chem. J.*, **15**, 471—493).—The salts used in these experiments were the potassium, sodium, ammonium, magnesium, calcium, and strontium chloracetates, and sodium bromacetate. A weighed quantity of the salt was heated with water, and the amount of decomposition determined at stated intervals of time by titration of the liberated glycollic acid with N/10 potash solution. The following conclusions are drawn from the experiments. (1.) The decomposition is greatly retarded by increasing the quantity of water. (2.) The decomposition is non-reversible, and can be carried to completion. (3.) The decomposition, at certain stages of dilution, probably at all, is independent of the nature of the base in the salt. (4.) The coefficients of velocity of the decomposition at N, N/3, and N/10 dilutions are inversely proportional to the coefficients of affinity of chloracetic and bromacetic acids at these dilutions. (5.) The decomposition reaches a minimum at a dilution somewhat above N/10, from which point to a dilution of 1,000 litres the decomposition is nearly constant. (6.) The velocity of decomposition is slightly accelerated by glycollic acid proportionately to the quantity of acid present. Other acids, feebler than chloracetic acid, have also been found to *accelerate* the decomposition in the order of their affinities. Acids stronger than chloracetic acid have the reverse effect. (7.) The velocity is also slightly accelerated by potassium chloride.

The views which the authors hold with regard to the reason for the decrease of velocity in the decomposition of these salts have already been set forth in the discussion on the decomposition of silver chloracetate (this vol., ii, 266). Ostwald (*Zeit. physikal. Chem.*, **11**, 431) has questioned the validity of the explanation there proffered; the authors fail, however, to discover any essential difference between their views and those of Ostwald on the subject.

It is noted in the experimental part of the paper, that when sodium bromacetate is heated with a small quantity of water, a little glycollide is always formed, and subsequently dissolves as glycollic acid. It would thus seem that in the decomposition of these salts by water, there is a secondary reaction to be taken into account.

A. G. B.

Thermochemistry of β-Dibromopropionic acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **24**, 615—620).—The modification of β-dibromopropionic acid melting at 51° evolves about 0·5 Cal. for a molecular proportion on passing into the modification melting at 63°. The heat of dissolution of the (? higher melting) acid is 4·0 Cal. at 13°, and the heat of neutralisation of a decinormal solution with decinormal potash is 15·4 Cal., a value much higher than that usually observed in the case of organic acids. The action of a decinormal solution of hydrochloric acid on an equivalent solution of potassium β-dibromopropionate is accompanied by the absorption of 0·96 Cal., whilst the opposite reaction was found to develop heat = 0·71 Cal.

Decinormal solutions of the acid and sodium acetate react with development of heat = 1·9 Cal. Solutions of the free acid and its potassium salt may be mixed without thermal effect. The potassium salt (1 mol.) is further acted on by potash (1 mol.) in decinormal solution, with development of heat = 13·4 Cal. and formation of potassium bromide. J. W.

Ethereal Oil from the Root of Aspidium filix mas. By A. EHRENBERG (*Arch. Pharm.*, **231**, 345—356).—The ethereal extract of the root of *Aspidium filix mas*—"oleum æthereum filicis"—is shown to owe its property as a cure for worms not to the filicic acid contained in it, but to the ethereal oil. The oil is obtained by steam distillation of the freshly-gathered air-dried roots, which yield in April, June, and September to November respectively, 0·008, 0·025, and 0·04—0·045 per cent. of ethereal oil. This oil contains 40 per cent. of free acids, chiefly of the fatty series from propionic to caproic; butyric acid was, however, the only one that could be identified with certainty. The rest of the oil was hydrolysed by heating it with alcoholic potash; among the products were hexyl and octyl alcohols, and probably some aromatic alcohol, perhaps belonging to the series of terpenes; and, besides these, acids of the fatty series from butyric to pelargonic, amongst which again butyric acid alone could be identified with certainty. C. F. B.

Combination of Oxalic acid with Titanic and Stannic acids. By E. PÉCHARD (*Compt. rend.*, **116**, 1513—1516).—Titanic acid, prepared by the action of sodium carbonate on a solution of titanium chloride, dissolves readily in a warm solution of potassium hydrogen oxalate, and when the liquid cools, *potassium oxalotitanate*,

$$2C_2O_4HK,TiO_2 + H_2O,$$

separates in colourless crystals which seem to belong to the triclinic system. It can be recrystallised from warm water, but is insoluble in alcohol, which precipitates it from aqueous solutions in slender, colourless needles. The salt is decomposed by alkalis, but the precipitation of the titanic acid is not complete. *Barium oxalotitanate*, $(C_2O_4H)_2Ba,TiO_2 + H_2O$, is obtained as a white, crystalline precipitate by the addition of a solution of barium chloride to a solution of the preceding salt. If a solution of the barium salt is exactly decomposed by sulphuric acid, and the liquid is allowed to evaporate in a vacuum,

oxalotitanic acid, $2C_2O_4H_2,TiO_2 + 2H_2O$, separates in acicular crystals, which effloresce rapidly and are insoluble in water or alcohol; the solution of this compound is strongly acid, but it does not combine readily with alkalis.

Gelatinous stannic acid likewise dissolves readily in a solution of potassium hydrogen oxalate, and on evaporation *potassium oxalostannate*, $2C_2O_4HK,SnO_2 + 5H_2O$, separates in white, monoclinic crystals, which rapidly effloresce, and are soluble in water but not in alcohol. The barium salt is formed in the usual way, and from it oxalostannic acid can be obtained. It crystallises in nacreous scales, less soluble in water than oxalotitanic acid.

Silica does not yield analogous compounds. C. H. B.

Action of Inorganic acid Metallic Oxides on Organic acids. By A. Rosenheim (*Zeit. anorg. Chem.*, **4**, 352—373).—Monobasic acids, such as formic, acetic, propionic, and benzoic acids, do not dissolve tungstic and molybdic acids. Oxalic acid dissolves both tungstic and molybdic acids. Malonic, succinic, and phthalic acids do not dissolve tungstic acid, and dissolve only a small quantity of molybdic acid. Bibasic and polybasic hydroxy-acids, such as malic acid, tartaric acid, &c., dissolve tungstic acid, although less readily than oxalic acid; but they easily dissolve molybdic acid. Monobasic hydroxy-acids, such as glycollic and lactic acids, behave like oxalic acid, but dissolve much smaller quantities of the metallic oxides. Salicylic acid dissolves only a small quantity of tungstic acid, but a considerable quantity of molybdic acid. Meta- and para-hydroxybenzoic acids are almost without action on molybdic acid. These results are in accordance with those obtained by Magnanini (Abstr., 1891, 251; 1892, 256, 1265).

Action of Tungstic acid on Oxalic acid and on Oxalates.—When an excess of tungstic acid is added to a boiling solution of oxalic acid and the mixture allowed to remain, a colloidal solution is obtained, which is yellow by transmitted light, and has a greenish-yellow fluorescence. It undergoes no change, even if kept for four months; on concentration, it deposits oxalic acid, and then entirely decomposes with precipitation of tungstic acid.

A *double salt* of the constitution $COOK\cdot COO\cdot WO_2\cdot OK + H_2O$ is obtained by dissolving tungstic acid in a solution of normal potassium oxalate. It crystallises in white, microscopic tablets, is very sparingly soluble in water, has an acid reaction, and, when boiled with strong hydrochloric or sulphuric acid, gives a precipitate of tungstic acid. When boiled with vanadic acid, it gives a deep yellow coloration. It is also easily obtained by boiling hydrogen potassium oxalate with the theoretical quantity of a melt of potassium carbonate and tungstic anhydride. The corresponding *sodium* and *ammonium* salts have been prepared; they are similar to the potassium salt, but are very soluble.

When tungstic acid is dissolved in solutions of the acid oxalates, crystalline mixtures of potassium ditungstate and acid potassium oxalate of the composition $x(K_2O,2C_2O_3) + y(K_2O,2WO_3)$ are obtained, from which hydrogen potassium oxalate can be separated by crystallisation.

Action of Molybdic acid on Oxalic acid and on Oxalates.—The acid

$\begin{matrix}COO\\COO\end{matrix}>MoO_2 + 3H_2O$ is obtained by boiling an excess of molybdic acid with a solution of oxalic acid, evaporating to a syrup, and then dissolving in a small quantity of water containing a few drops of nitric acid. The compound has already been described by Péchard (Abstr., 1889, 858).

Two compounds are obtained by saturating a boiling solution of ammonium oxalate with molybdic acid. The one crystallises in sparingly soluble crusts, decomposes on recrystallisation, and has the composition $C_2O_2(O{\cdot}MoO_2{\cdot}ONH_4)_2$; the other forms easily soluble, white needles, can be recrystallised without decomposition, and gives a yellow coloration when boiled with vanadic acid. It has the constitution $COONH_4{\cdot}COO{\cdot}MoO_2{\cdot}ONH_4 + H_2O$.

When potassium oxalate is boiled with an excess of molybdic acid, potassium trimolybdate is formed, together with a small quantity of the *salt* $K_2O,MoO_3,C_2O_3 + H_2O$. The latter is easily obtained by boiling potassium molybdate with oxalic acid in molecular proportion.

The *salt*, $K_2O,2MoO_3,C_2O_3$, is obtained by dissolving a melt of potassium carbonate (1 mol.) with molybdic anhydride (2 mols.) in a solution of oxalic acid (1 mol.). It crystallises in sparingly soluble white crusts.

Sodium oxalate reacts with molybdic acid in the same way as the potassium salt. The *salt* $COONH_4{\cdot}COO{\cdot}MoO_2{\cdot}ONa + 2H_2O$ is obtained by the action of hydrogen ammonium oxalate (1 mol.) on sodium dimolybdate (1 mol.). It crystallises in large, lustrous prisms.

The *salt* $COONH_4{\cdot}COO{\cdot}MoO_2{\cdot}OH + H_2O$ is obtained by boiling an excess of molybdic acid with hydrogen ammonium oxalate. It crystallises in prisms, and does not reduce vanadic acid. The corresponding *potassium salt* is obtained in a similar way. The *sodium salt* could not be obtained.

Action of Vanadic acid on Normal Oxalates.—When vanadic acid is boiled with solutions of normal alkali oxalates, deep yellow solutions are obtained, which, on concentration, deposit red acid vanadates and large yellow prisms of oxalovanadates. The two compounds are separated mechanically.

The *ammonium salt*, $3(NH_4)_2O,V_2O_5,4C_2O_3 + 4H_2O$, the *potassium salt*, $3K_2O,V_2O_5,4C_2O_3 + 6H_2O$, and the *sodium salt*, $3Na_2O,V_2O_5,4C_2O_3 + 6H_2O$ have been prepared. The author assigns to them the constitution $V_2O_2(OR)_2(O{\cdot}CO{\cdot}COOR)_4 + xH_2O$. They are easily obtained pure by the action of 1 mol. of a normal vanadate, $R_2OV_2O_5$, on 4 mols. of an acid oxalate. E. C. R.

Preparation of Amylic Pyruvate. By L. Simon (*Bull. Soc. Chim.* [3], **9**, 136—137).—*Amylic pyruvate*, $CH_3{\cdot}CO{\cdot}COO{\cdot}C_5H_{11}$, is prepared by heating a mixture of amyl alcohol with anhydrous pyruvic acid in molecular proportion for several hours in a reflux apparatus under reduced pressure; the product is then slowly distilled from the water bath under a pressure of 10—15 mm., using a fractionating column. The yield is 99 per cent. of the theoretical. J. B. T.

Synthesis of a Lactone from Formaldehyde and Pyruvic acid. By H. Hosaeus (*Annalen*, **276**, 79—82).—The *lactone* $O\begin{array}{l}\text{———}CH_2\\ |\\ CO\cdot CH(OH)\end{array}>C(CH_2\cdot OH)_2$, is prepared by heating pyruvic acid (1 mol.) with formic acid (4 mols.) in presence of water and calcium hydroxide; it crystallises from alcohol in white prisms, melts at 184°, and is very easily soluble in water. When boiled with alkalis, it yields salts of the acid $C_6H_{12}O_6$. The *calcium* salt is a micro-crystalline substance. Unlike pyruvic acid, the lactone does not yield a compound with phenylhydrazine, and it furnishes no iodoform when treated with iodine and soda. A. R. L.

Synthesis of a Lactone from Formaldehyde and Levulinic acid. By P. Rave and B. Tollens (*Annalen*, **276**, 69—75).—The *lactone* $C_{10}H_{16}O_6$ is obtained by keeping a mixture of levulinic acid (50 grams), 40 per cent. formaldehyde (250 grams), water (5 litres), and barium hydroxide (200 grams) for 14 days with frequent shaking, subsequently heating it to boiling, removing the barium by means of sulphuric acid, and evaporating the filtrate, when it separates in rhombic tablets. It has a bitter taste, melts at 174—176°, and emits a penetrating odour when ignited on platinum foil. A molecular weight determination by the cryoscopic method showed that the above is the molecular formula. The *triacetyl* derivative, $C_{10}H_{13}O_3(OAc)_3$, melts at 161°. The authors submit the following constitutional formula for the lactone,

$$O<\begin{array}{l}CH_2\\ CH_2\end{array}>C<\begin{array}{l}CH[C(CH_2\cdot OH)_3]\\ CH_2\text{————}CO\end{array}>O.$$ A. R. L.

Preparation of Mucic acid from Gum Arabic. By E. Maumené (*Bull. Soc. Chim.* [3], **9**, 138—142).—The variable yield of mucic acid is partly attributable to the fact that little attention is generally paid to the concentration and proportion of the nitric acid employed, and partly to the actual condition of the gum. The author discusses the first of these points at length, and gives details of previous work on the subject; he considers that gum arabic is a mixture of two varieties, which he designates by α- and γ-; both of these undergo condensation on heating or by the action of sulphuric acid, and it is from this condensation compound that mucic acid is chiefly or wholly obtained. By previously heating the gum at 165° and treating it with a dilute nitric acid not in large excess, it yielded as much as 65—69 per cent. of mucic acid. Both "condensed" and "uncondensed" gum are present in wine residues, and it is possible that the above facts may throw light on the difficulty of obtaining a constant weight of wine residues at 100°. J. B. T.

Ethylic Acetoacetate. By J. U. Nef (*Annalen*, **276**, 200—245; compare Abstr., 1892, 140).—By the action of benzoic chloride on the metallic derivatives of ethylic acetoacetate there are obtained ethylic acetoacetate, ethylic α-benzoyl-β-hydroxyisocrotonate, ethylic dibenzoylacetoacetate, and ethylic β-benzoxyisocrotonate,

OBz·CMe:CH·COOEt.

The last-named compound crystallises in colourless needles, melts at 43°, decomposes when heated with alcoholic sodium ethoxide into ethylic benzoate and ethylic sodacetoacetate, and yields β-benzoylphenylhydrazine and, perhaps, phenylmethylpyrazolone when treated with an ethereal solution of phenylhydrazine; when bromine is added to its solution in chloroform, cooled to −15°, a dibromide appears to be first formed, but hydrogen bromide is subsequently liberated, and the final products are ethylic bromacetoacetate and benzoic bromide.

The neutral compound formed by the action of acetic chloride on the metallic derivatives of ethylic acetoacetate is not ethylic triacetylacetate as previously stated (*loc. cit.*), but *ethylic β-acetoxyisocrotonate*, OAc·CMe:CH·COOEt. The compound absorbs bromine (1 mol.) at −15°, but soon afterwards hydrogen bromide is evolved, and the ultimate products are ethylic α- and γ-bromacetoacetate and acetic bromide. Ethylic β-acetoxyisocrotonate is also formed on boiling ethylic acetoacetate with acetic anhydride.

The author confirms Claisen's observation (Abstr., 1892, 1070) that his so-called ethylic acetylcarbintricarboxylate (*loc. cit.*) is *ethylic β-carbethoxyisocrotonate* (ethylic carboxyethylacetoacetate). This compound absorbs bromine (1 mol.) at −10°, but the *dibromide* produced is partially decomposed on distillation even under diminished pressure.

Ethylic β-carbethoxyacrylate, COOEt·CH:CH·O·COOEt, is obtained by treating ethylic sodioformylacetate suspended in ether with ethylic chlorocarbonate in the cold; it is a colourless oil having a pleasant odour, boils at 135° under a pressure of 25 mm., dissolves without alteration in nitric acid of 1·5 sp. gr., and forms a fairly stable *dibromide*.

Ethylic acetoxyfumarate, $\begin{matrix}\mathrm{COOEt\cdot C\cdot OAc}\\ \|\\ \mathrm{H\cdot C\cdot COOEt}\end{matrix}$, is the portion of the product insoluble in alkali obtained when acetic chloride is added to ethylic sodoxalacetate suspended in ether; it boils at 150° under a pressure of 18 mm., and is decomposed by sodium ethoxide and ethylic acetate and ethylic sodoxalacetate; it absorbs bromine (1 mol.) at −15°, but the *dibromide* decomposes yielding ethylic α-bromo-β-hydroxyfumarate (Wislicenus' ethylic bromoxalacetate, Abstr., 1890, 133). The portion which is soluble in alkalis of the above-mentioned product of the action of acetic chloride on ethylic sodoxalacetate, is a mixture of ethylic oxalacetate and *ethylic α-acetyl-β-hydroxyfumarate*, $\begin{matrix}\mathrm{COOEt\cdot C\cdot OH}\\ \|\\ \mathrm{Ac\cdot C\cdot COOEt}\end{matrix}$. The latter is a colourless oil, boils at 134—136° under a pressure of 10 mm., and decomposes carbonates in the cold; an alcoholic solution gives a deep red coloration with ferric chloride. Compounds similar to those just described are obtained from ethylic sodoxalacetate and benzoic chloride. Ethylic oxalacetate is identical with ethylic hydroxyfumarate, for the author finds that the above-described ethylic acetoxyfumarate is obtained from it by direct acetylation. When ethylic oxalacetate is treated with phosphoric chloride at 50°, ethylic chloro-

fumarate is obtained, which, when hydrolysed with alcoholic potash, yields chlorofumaric acid (Perkin, Trans., 1888, 697).

Ethylic ethoxyfumarate, $\begin{matrix}\mathrm{COOEt\cdot C\cdot OEt}\\ \|\\ \mathrm{H\cdot C\cdot COOEt}\end{matrix}$, obtained by gradually adding ethylic iodide to the silver derivative of ethylic oxalacetate, is an oil of pleasant odour; its sp. gr. is 1·06 at 22°, it boils at 130° under a pressure of 11 mm. or at 136° under 16 mm. pressure. It gives no coloration with ferric chloride, and differs, therefore, from ethylic α-ethyl-β-hydroxyfumarate (Arnold, *Annalen*, **246**, 337; Abstr., 1888, 1179). The compound absorbs bromine (1 mol.) at −15°, and on distilling the *dibromide*, it decomposes into ethylic α-bromo-β-ethoxyfumarate boiling at 160° under a pressure of 17 mm., and apparently ethyl bromovinyl ether, carbonic anhydride being evolved.

When an alcoholic solution of ethylic ethoxyfumarate is treated in the cold with sodium ethoxide (2 mols.), the sodium salt which separates is dissolved in water, and the solution acidified, *hydroxyfumaric acid*, $\begin{matrix}\mathrm{COOH\cdot C\cdot OH}\\ \|\\ \mathrm{H\cdot C\cdot COOH}\end{matrix}$, is obtained; it melts at 172° with decomposition, and its aqueous solution gives a dark red coloration with ferric chloride; when treated with phenylhydrazine hydrochloride in aqueous solution, phenylpyrazolonecarboxylic acid (Wislicenus, Abstr., 1888, 1178) is formed.

When the silver derivative of ethylic α-acetyl-β-hydroxyisocrotonate is suspended in ether and treated in the dark with ethylic iodide, the portion of the product soluble in alkalis consists chiefly of ethylic α-acetylacetoacetate. When the portion which is insoluble in alkalis is heated on the water-bath with alcoholic sodium ethoxide, it gives Friedrich's ethoxyisocrotonic acid (*Annalen*, **219**, 328), but if treated in the cold with the same reagent, an oil is obtained boiling at 190—195°, and having the odour of ethylic α-ethylacetoacetate. A lengthy discussion of these results concludes the paper. A. R. L.

Organic Electrosyntheses. By S. P. Mulliken (*Amer. Chem. J.*, **15**, 523—533; compare Crum Brown and Walker, Abstr., 1891, 1192).—The compounds chosen for this investigation are the ketonic derivatives, like acetylacetone and ethylic acetoacetate. The products obtained by the electrolysis of such compounds are formed by the combination of the anions, so that they are identical with products which are obtained by treating the silver or sodium derivatives of the same compounds with iodine. The electrolytic cell consisted of a glass cylinder surrounded by a water cooler, rendered necessary by the high resistance of the electrolyte. The anodes were spirals of platinum wire, 1—2 mm. in diameter, and the cathodes rectangular strips of platinum foil, almost wide enough, when folded into cylinders, to surround the anodes. The current used was $\frac{1}{15}$—$\frac{1}{3}$ ampère.

The electrolysis of diethylic sodiomalonate yields tetrethylic ethanetetracarboxylate. Ethylic sodiomethanetricarboxylate yields *hexethylic ethanehexacarboxylate*, $\mathrm{C(COOEt)_2\cdot C(COOEt)_2}$, which forms white crystals, melts at 101° (corr.) and is freely, but slowly, soluble in alcohol and in ether.

The electrolysis of acetylacetone might be expected, if Perkin's views as to its hydroxyketonic character (Trans., 1892, 816) be correct, to yield a "tetracetylethane." The compound actually obtained is provisionally termed *tetracetylethane* by the author, and is regarded as having the constitution $\begin{matrix}OH\cdot CMe{:}C\cdot COMe\\ |\\ OH\cdot CMe{:}C\cdot COMe\end{matrix}$. It crystallises in colourless cubes, melts at 191·2° (corr.), and is very sparingly soluble in cold alcohol. It is a feeble acid, and readily absorbs bromine. The same compound was prepared by treating the sodium derivative of acetylacetone with iodine, and its constitution was, to a certain extent, confirmed by the formation of condensation products; thus, when boiled with ammonium acetate solution, and then with dilute sulphuric acid and a pine-splinter, it yields Knorr's pyrroline reaction, showing that 5 : 2-dimethyl-3 : 4-diacetylpyrroline has been formed. So, also, on treatment with strong sulphuric acid, it yields the condensation product 2 : 5-*dimethyl*-2 : 3-*diacetylfurfuran*, which crystallises in white, felted needles, melts at 63°, and dissolves in boiling water.

The electrolysis of ethylic acetoacetate might be expected to yield ethylic diacetosuccinate, for this compound is the product of the action of iodine on the sodium derivative. It was found difficult to isolate the ethylic diacetosuccinate from the other products of the electrolysis, but it was undoubtedly present. A. G. B.

Nitrogen Halogen Compounds. By F. Lengfeld and J. Stieglitz (*Amer. Chem. J.*, **15**, 504—518).—The authors prepared *methylic methocarboxyl-β-amidopropionate*, $COOMe\cdot NH\cdot CH_2\cdot CH_2\cdot COOMe$, from methylic β-amidopropionate and methylic chloroformate, and found that it is identical with the main product of the action of sodium methoxide and methyl alcohol on bromosuccinimide (methylic methoxysuccinamic acid, this vol., i, 310), whose constitution is thus settled. When this compound is treated with hydrochloric acid, *β-amidopropionic acid hydrochloride*, $HCl,NH_2\cdot CH_2\cdot CH_2\cdot COOH$, is produced; it forms white, irregular plates, and melts at 122·5°. β-Amidopropionic acid melts, with decomposition, at 206° (Hoogewerff and Van Dorp, Abstr., 1891, 1216, give 196°; Mulder gives 180°); an improvement in Hoogewerff and Van Dorp's method for preparing this acid (*loc. cit.*) is described. The *sulphate* of this acid crystallises in short, thick prisms, melts, with some decomposition, at 150°, and dissolves easily in water, but only sparingly in alcohol.

Methylic β-amidopropionate *hydrochloride* crystallises in lustrous, hygroscopic scales, and melts at 94—95°. The hydrochloride of the ethylic salt crystallises in white plates, melts at 65·5°, and dissolves easily in water, alcohol, and chloroform.

Methocarboxyl-β-amidopropionic acid has already been described as methoxysuccinamic acid (this vol., i, 310). The *barium* and *silver* salts are described; the *ethylic* salt is a colourless oil which solidifies in a freezing mixture, and melts at 15·5°. The *amide*,

$$COOMe\cdot NH\cdot CH_2\cdot CH_2\cdot CONH_2,$$

crystallises in colourless, broad, orthorhombic plates, with sharply defined lines of cleavage; it melts at 142·5°.

Methylic ethocarboxyl-β-amidopropionate,

$$COOEt{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}COOMe,$$

prepared by treating methylic β-amidopropionate hydrochloride with silver oxide and ethylic chloroformate, is an oil which boils at 134—137° (15 mm.), and melts below 0°. The *acid* itself forms colourless crystals, melting at 59°. The *amide* also forms colourless crystals, and melts at 120·5°.

Dimethylic succino-β-ureïdopropionate,

$$COOMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}COOMe,$$

melts at 65·5°. By mild hydrolysis, it yields succinic acid and β-ureïdopropionic acid. Concentrated hydrochloric acid decomposes it into succinic acid and β-lactylcarbamide.

Methylic β-ureïdopropionate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}COOMe$, is obtained by the action of potassium cyanate on methylic amidopropionate hydrochloride; it forms colourless, long, flat prisms, melts at 66·5°, and is easily soluble in water, alcohol, and chloroform. *β-Ureïdopropionic acid* melts with evolution of gas at 170—171°; it is very unstable, readily losing water with formation of β-lactylcarbamide; the *potassium* salt was prepared and found to be very hygroscopic, and to melt at 100°.

β-Lactylcarbamide, $\begin{matrix}CH_2{\cdot}NH{\cdot}CO\\ |\\ CH_2{\cdot}CO{\cdot}NH\end{matrix}$, melts at 272° with decomposition; it is neutral and insoluble in sodium carbonate, but soluble in caustic alkalis. The *silver* derivative, $\begin{matrix}CH_2{\cdot}NH{\cdot}CO\\ |\\ CH_2{\cdot}CO{\cdot}NAg\end{matrix}$, was prepared.

A. G. B.

Amidomaleamide and Oxysuccinamide. By R. T. Mamert (*Compt. rend.*, **117**, 167—170).—Amidomaleamide,

$$CONH_2{\cdot}C(NH_2){:}CH{\cdot}CONH_2,$$

is formed by the action of aqueous ammonia on ethylic chlorofumarate in the cold; after two days, the amide crystallises out in dull, opaque, yellowish, prismatic crystals, melting, with decomposition, at 190—195°. It is decomposed by hot alkalis, and is hydrolysed by cold alkalis into the *alkali amidomaleamate*, $CONH_2{\cdot}C(NH_2){:}CH{\cdot}COOR$. The corresponding *copper salt* is described. When treated with hot aqueous phenylhydrazine acetate, ammonia is eliminated, and *phenylhydrazosuccinamide*, $NHPh{\cdot}N{:}C(CONH_2){\cdot}CH_2{\cdot}CONH_2$, is formed; this crystallises in colourless needles, is optically active, and melts, with decomposition, at 180°. When amidomaleamide is hydrolysed with dilute sulphuric acid, it is transformed into *oxysuccinamide*,

$$CONH_2{\cdot}CO{\cdot}CH_2{\cdot}CONH_2,$$

which crystallises in small, colourless needles, and melts, with decomposition, at 180°. It gives a characteristic red coloration with ferric chloride, and with copper sulphate and phenylhydrazine acetate, yields the amidomaleamate and hydrazone mentioned above. Sodium amalgam converts it into malic acid.

Jn. W.

Essential Oil of Cochlearia armoracia. By G. Sani (*Real. Accad. Linc.*, 1892, ii, 17—18).—A glucoside contained in *Cochlearia armoracia* undergoes hydrolysis when the bruised roots, gathered during the autumn or winter, are left for 24 hours in contact with water; the essential oil and a little sulphur are then extracted with ether. On evaporating the ethereal solution, a residue of allylthiocarbimide is obtained; the roots therefore contain potassium myronate. W. J. P.

Isomeric Thetines. By G. Carrara (*Gazzetta*, **23**, i, 493—509; compare Brown and Letts, *Trans. Edin. R. Soc.*, **28**, 561).—*Methylethylthetine bromide*, $SMeEtBr{\cdot}CH_2{\cdot}COOH$, is readily prepared by the action of bromacetic acid on methylic ethylic sulphide in the cold; it forms highly deliquescent, rhombohedral-shaped crystals melting at 84° with decomposition, and is soluble in alcohol, but not in ether or benzene. It has an acid reaction, and is shown by cryoscopic determinations to undergo dissociation in aqueous solution. The corresponding *platinochloride*, $(C_5H_{10}O_2S)_2,H_2PtCl_6$, forms red, orthorhombic crystals, $a : b : c = 0{\cdot}9462 : 1 : 1{\cdot}0133$, which melt at 167° with decomposition. *Methylethylthetine*, $SMeEt<^{-O-}_{CH_2}>CO$, is obtained by treating the aqueous solution of its bromide with moist silver oxide, and distilling off the water under reduced pressure. It is a white, deliquescent substance, and is neutral to litmus; cryoscopic experiments in water and acetic acid, and boiling point determinations of alcoholic solutions, seem to indicate that the anhydride does not become hydrated in aqueous solution.

Dimethyl-α-propionylthetine bromide, $SBrMe_2{\cdot}CHMe{\cdot}COOH$, an isomeride of the preceding bromide, is obtained from methylic sulphide and α-bromopropionic acid. It forms small, rectangular tablets melting at 84—85° with decomposition, and is very deliquescent; cryoscopic determinations show it to be completely dissociated in aqueous solutions. The *platinochloride*, $(C_5H_{10}O_2S)_2,H_2PtCl_6.2H_2O$, forms monosymmetric prisms, $a : b : c = 2{\cdot}313 : 1 : 3{\cdot}051$; $\beta = 83° 23'$, which melt at 105—106°. Its purification is difficult, owing to intermixture with the platinochlorides of dimethylethylsulphine and trimethylsulphine; these sulphines are produced by decomposition of the thetine during the evaporation of its aqueous solution. *Dimethyl-α-propionylthetine*, $SMe_2<^{-O-}_{CHMe}>CO$, is obtained by treating the aqueous solution of the bromide with moist silver oxide; it is a very deliquescent, white substance, and gives similar results to its isomeride in cryoscopic determinations.

Dimethyl-β-propionylthetine bromide, $C_5H_{11}O_2SBr$, is prepared by heating a mixture of β-bromopropionic acid and methylic sulphide. It is less deliquescent than its isomerides, and forms beautiful, white needles which melt at 115° with decomposition. The *platinochloride*, $(C_5H_{10}O_2S)_2,H_2PtCl_6$, crystallises in anhydrous anorthic needles, $a : b : c = 1{\cdot}087 : 1 : 1{\cdot}071$; $\alpha = 77° 35'$, $\beta = 121° 42'$, $\gamma = 101° 31'$. The thetine itself could not be prepared in a pure state, being much less stable than its isomerides. W. J. P.

Synthesis of Mercaptothiazoles. By A. MIOLATI (*Gazzetta*, **23**, i, 575—580).—The author has succeeded in synthesising the mercaptothiazoles by an extension of the process by which he determined the constitution of the so-called rhodanic acid (Abstr., 1891, 943); the new method depends on a condensation of the α-halogenated ketones with ammonium dithiocarbamate.

Ethylic methylmercaptothiazolecarboxylate, $N\begin{matrix}C(SH)\cdot S\cdot COOEt\\ \|\\ CMe{=}C\end{matrix}$, is obtained on heating ammonium dithiocarbamate with ethylic chloracetoacetate; it forms white needles melting at 141°, and is insoluble in water, but soluble in alcohol or ether. Its alcoholic solution precipitates salts of silver and mercury. On dissolving it in potash and acidifying the solution, the corresponding *acid* separates; it is obtained as a crystalline powder which melts at 211—212° with decomposition, and is soluble in alcohol, ether, or boiling water.

On heating ammonium dithiocarbamate with chloracetone in alcoholic solution, *methylmercaptothiazole*, $N\begin{matrix}C(SH)\cdot S\\ \|\\ CMe{=}CH\end{matrix}$, is obtained; it melts at 89—90°, and is soluble in the ordinary organic solvents.

Phenylmercaptothiazole, $N\begin{matrix}C(SH)\cdot S\\ \|\\ CPh{=}CH\end{matrix}$, is prepared by the action of ammonium dithiocarbamate on bromacetophenone; it forms monosymmetric crystals which melt at 168°. It is accompanied by a substance melting at 114°, possibly dithiocarbamineacetophenone.

W. J. P.

Condensation of Aliphatic Alcohols with Aromatic Hydrocarbons. By A. BROCHET and P. LE BOULENGER (*Compt. rend.*, **117**, 235—238).—When benzene (1 part) is heated with alcohol (2 parts) and sulphuric acid (4 parts) in a sealed tube at 175—200° for 3—4 hours, ethylbenzene, boiling at 137°, and hexethylbenzene, melting at 123°, are formed. Similar results are obtained with normal propyl alcohol, hexapropylbenzene, melting at 118°, being formed, as well as liquid hydrocarbons, boiling at 210—240°. The yield of mixed hydrocarbons is 50 per cent. Isobutyl alcohol yields a butylbenzene, boiling at 167—168°, and a dibutylbenzene, boiling at 230—240°. The mechanism of the reaction appears to be exhibited in the case of hexyl alcohol, benzenesulphonic acid being formed, and recognised by conversion into its calcium salt and into phenol. The hydrogen hexylic sulphate first formed appears to react with the benzene according to the equation

$$OH\cdot SO_2\cdot OC_6H_{13} + 2C_6H_6 = C_6H_5\cdot SO_3H + C_6H_5\cdot C_6H_{13} + H_2O.$$

Hydrogen alkylic sulphates, however, when separately prepared, do not seem to have any such action on benzene; neither do the aromatic sulphonic acids react with the alcohols.

JN. W.

Ethereal Oil of the Seeds of Cicuta virosa. By J. TRAPP (*Arch. Pharm.*, **231**, 212—213).—In 1858 the author prepared an ethereal oil by distillation of the dried seeds of *Cicuta virosa* with

water; it resembles Roman cumin oil in taste and odour, and consists chiefly of cymene and cuminaldehyde. J. B. T.

Condensation of Hydrocarbons of the Benzene Series with those of the Ethylene Series. By A. Brochet (*Compt. rend.*, **117**, 115—118).—Crystallisable benzene is mixed with a small quantity of normal α-hexylene and agitated with about 10 per cent. of ordinary sulphuric acid; development of heat and evolution of sulphurous anhydride ensue, and the liquid blackens. When the action ceases, a further quantity of hexylene is added, and this process is continued until 1 part of hexylene has been added for every 2 parts of benzene. The acid must be renewed at least once towards the end of the operation. The upper layer of liquid is decanted and washed first with water and afterwards with sodium hydroxide solution, and fractionated; the product is hexylbenzene, formed simply by direct combination, and the yield is about 50 per cent. It is a colourless, mobile liquid, boiling at 208° under ordinary pressure; sp. gr. at 15°/4° = 0·869; refractive index $n = 1·492$; molecular refractive power (new formula) = 53·93. It combines with bromine in the cold, with immediate evolution of hydrogen bromide. It yields a monosulphonic acid, the barium salt of which crystallises with $2H_2O$ in large, nacreous lamellæ, soluble in water or alcohol, especially on heating. The calcium salt is similar.

Hexylbenzene reduces potassium manganate and permanganate slowly in the cold, and more rapidly on heating; the molecule seems to be completely broken up, and only a small quantity of oxalic acid is obtained. Nitric acid, somewhat diluted, yields benzoic acid, and if the hydrocarbon is allowed to fall drop by drop into a boiling solution of chromic acid mixture, formic acid is one of the products of oxidation. It would seem, therefore, that this hexylbenzene is methylbutyltoluene or methylbutylphenylmethane.

This method of synthesis is a general one. Toluene behaves like benzene, but amylene gives less satisfactory yields than hexylene.

C. H. B.

Identity of the Hydrocarbon C_7H_{14} derived from Perseïtol and from Resin Oil with Heptanaphthene. By L. Maquenne (*Bull. Soc. Chim.* [3], **9**, 129—131).—The hydrocarbon C_7H_{14} is shown to be identical with heptanaphthene from Russian petroleum by a comparison of their colour reactions and physical constants; the former compound has, however, been shown to be hexahydrotoluene (compare Abstr., 1892, 1065), and it is also identical with that from essence of resin and with Markovnikoff's hydrocarbon from suberonyl alcohol (this vol., i, 13). Heptine is therefore a methylcyclohexane.

J. B. T.

A Decanaphthene from Caucasian Petroleum. By W. Rudevitsch (*J. pr. Chem.* [2], **48**, 188—191).—The production of terpenes from naphthenes has not heretofore been effected; the author has again attempted it. A decanaphthene (b. p. 168—170°; sp. gr. at 0°/0° = 0·8073) was chlorinated, whereby two chlorides, boiling respectively at 213—215° and 215—218°, and of sp. gr. at 0°/0° of 0·9574 and 0·9644, were obtained. Both these chlorides were con-

verted into naphthylenes, which boiled at 167—168° and 169—172° respectively; the former resembles Berkenheim's menthene (Abstr., 1892, 866). Besides these naphthylenes, *decanaphthenyl acetate*, $CH_3{\cdot}COOC_{10}H_{19}$, was prepared; it is colourless, viscid, and of fruity odour; it boils at 237·5—239·5° (corr.), and its sp. gr. at 0°/0° is 0·9323. On hydrolysis, it yields *decanaphthene alcohol*, which is colourless, viscid, and of characteristic odour; its sp. gr. at 0°/0° is 0·9064, and it boils at 223·5—225·5° (corr.); the action of carbanil on this alcohol gives rise to vitreous needles which melt at 232—234°.

To obtain a $C_{10}H_{16}$ hydrocarbon, the two naphthylenes were mixed, converted into dibromides, and distilled with quinoline, but the original hydrocarbons were regenerated. When menthene dibromide is similarly treated, it yields a $C_{10}H_{16}$ hydrocarbon identical with that obtained from the same bromide by treatment with alcoholic potash (Berkenheim, *loc. cit.*). When the naphthylene boiling at 167—169° was heated with cupric sulphate according to Brühl's method (Abstr., 1892, 200), a hydrocarbon, $C_{20}H_{16}$ (b. p. 173—176°), was isolated.

The above reactions go to prove that the decanaphthene from petroleum is not identical with Berkenheim's menthonaphthene (Abstr., 1892, 866). A. G. B.

Structure of Nitro-compounds and of the Oxides of Nitrogen. By A. L. Potilitzin (*J. Russ. Chem. Soc.*, **25**, 75—79).—The author considers it probable that aromatic nitro-compounds are derivatives of nitric acid, and contain the group $-N\lessdot^{O}_{O}$; whilst fatty nitro-compounds are derived from nitrous acid, containing the group $-N<^{O}_{O}$. Nitroles and nitrolic acids he considers to be derivatives of hyponitrous acid, with the group —N:O. J. W.

Derivatives of Paratertiarybutylphenol. By K. Jedlicka (*J. pr. Chem.* [2], **48**, 97—112).—Dinitroparatertiarybutylphenol (m. p. 93°; Abstr., 1881, 898) has the constitution

$$[CMe_3 : (NO_2)_2 : OH = 4 : 2 : 6 : 1],$$

for when treated with concentrated nitric acid it yields picric acid. The *methyl* derivative of this phenol, $CMe_3{\cdot}C_6H_2(NO_2)_2{\cdot}OMe$, crystallises in pale-yellow laminæ, melts at 101—102°, and dissolves easily in hot alcohol but not in water; when heated with aqueous ammonia at 120—130°, it affords a good yield of the corresponding dinitrobutylaniline (Abstr., 1888, 823). The *ethyl* derivative is similar in properties, but melts at 95—96°.

Triamidotertiarybutylbenzene $[CMe_3 : (NH_2)_3 = 4 : 2 : 6 : 1]$, resulting from the reduction of the dinitrobutylaniline, crystallises in flat, colourless prisms, which become brown on exposure to the air; it melts at 156—157° and dissolves in alcohol and in ether, but only sparingly in water; it is a bi-acid base. The *hydrochloride*, $C_{10}H_{17}N_3,2HCl$, and *oxalate*, $C_{10}H_{17}N_3,C_2H_2O_4$, are described.

Triacetamidotertiarybutylbenzene $[CMe_3 : (NHAc)_3 = 4 : 2 : 6 : 1]$

crystallises in colourless needles, melts at 220°, and dissolves freely in alcohol, but only sparingly in water and benzene.

As the amido-groups in this triamidobutylbenzene are adjacent, the compound condenses easily with orthodiketones to form phenazines. *Phenanthramidotertiarybutylphenazine*, $\begin{matrix}C_6H_4\cdot C:N\\ |\\ C_6H_4\cdot C:N\end{matrix}>C_6H_2(CMe_3)\cdot NH_2$, forms orange-red needles, melts at 219—220°, and dissolves in hot alcohol, ether, and benzene, but not in water. *Benzilamidotertiarybutylphenazine*, $C_2N_2Ph_2{:}C_6H_4(CMe_3)\cdot NH_2$, crystallises in yellow needles, melts at 124—125°, and resembles the preceding phenazine in its behaviour towards solvents.

Nitrodiamidotertiarybutylbenzene crystallises in red needles, melts at 104—105°, and dissolves sparingly in water, but freely in alcohol or ether. It is a feeble, mon-acid base; the *hydrochloride*,

$$C_{10}H_{15}N_3O_2,HCl,$$

and *sulphate*, $(C_{10}H_{15}N_3O_2)_2,H_2SO_4$, are described. With orthodiketones, it yields phenazines such as *phenanthronitrotertiarybutylphenazine*, $C_{12}H_6{:}C_2N_2{:}C_6H_2(CMe_3)\cdot NO_2$, which crystallises in yellowish needles, melts at 235—236°, and dissolves freely in benzene; and *benzilnitrotertiarybutylphenazine*, $C_2N_2Ph_2{:}C_6H_2(CMe_3)\cdot NO_2$, which forms brownish, lustrous laminæ, melts at 195—196°, and behaves similarly towards solvents.

By azotising the diamido-compound, *nitrazimidotertiarybutylbenzene*, $CMe_3\cdot C_6H_2(NO_2)<\begin{matrix}NH\\ |\\ N\end{matrix}>N$, is obtained; this crystallises in flesh-coloured laminæ, melts at 205° (later, the m. p. 210—211° is given), and dissolves freely in alcohol and benzene, but not in water; it is feebly acid, yielding a crystalline *sodium* derivative, $C_{10}H_{11}NaN_4O$.

By treatment with acetic chloride, the nitrodiamidobutylbenzene yields *nitrotertiarybutylphenylenethenylamidine*,

$$CMe_3\cdot C_6H_2(NO_2)<\begin{matrix}NH\\ |\\ N\end{matrix}>CMe,$$

which forms brownish prisms, melts at 258°, and dissolves sparingly in water, but freely in alcohol and in ether. The *hydrochloride*, $C_{12}H_{15}N_3O_2,HCl$, was analysed. When concentrated formic acid is substituted for acetic chloride, *nitrotertiarybutylphenylenemethenylamidine*, $CMe_3\cdot C_6H_2(NO_2)<\begin{matrix}NH\\ |\\ N\end{matrix}>CH$, is obtained; this crystallises in pale-brown tables and prisms, melts at 261°, and has the same solubility as the ethenyl base. With benzoic chloride, *dibenzoyldiamidonitrotertiarybutylbenzene*, $CMe_3\cdot C_6H_2(NHBz)_2\cdot NO_2$, is obtained; this crystallises in white needles, melts at 245—246°, and dissolves in hot alcohol but not in water. A. G. B.

Action of Sulphuric Acid on Catechol and on Homocatechol. By H. Cousin (*Compt. rend.*, **117**, 113—115).—When catechol is allowed to remain for several days in contact with twice its weight of concentrated sulphuric acid, it yields a monosulphonic acid, $C_6H_3(OH)_2\cdot SO_3H$, the barium salt of which crystallises with $4H_2O$ in

small, rectangular prisms, soluble in water, but only slightly soluble in alcohol, whilst the potassium salt crystallises in anhydrous, silky needles, very soluble in water, but insoluble in cold alcohol. With ferric chloride, the solutions give a green coloration. The free acid crystallises in stellate groups of slender needles, which melt at 53—54°, are very deliquescent, dissolve in water and alcohol, and darken rapidly when exposed to light. This acid seems to be isomeric with that obtained by Barth and Schmidt by the action of fused potassium hydroxide on one of the disulphonated phenols.

When heated with sulphuric acid at 130°, catechol is partly decomposed, but, if heated for half an hour on a water bath with 5 parts of sulphuric acid containing 30 per cent. of the anhydride, it yields a disulphonic acid, $C_6H_2(OH)_2(SO_3H)_2$, which, when strongly cooled, crystallises in stellate groups of needles. The potassium salt crystallises with $1H_2O$ in small, oblique prisms, very soluble in water, but only slightly so in alcohol. The barium salt forms microscopic prisms, very slightly soluble in cold water, but somewhat more so in hot water.

Homocatechol yields only a monosulphonic acid even when the temperature and the proportion of sulphuric acid are varied, or if an acid containing 30 per cent. of anhydride is used. It crystallises in long needles melting at 93—94°, is deliquescent, very soluble in alcohol or ether, and becomes brown when exposed to light. The best results are obtained by heating the homocatechol on the water bath for four hours with twice its weight of sulphuric acid containing 30 per cent. of the anhydride. The barium salt crystallises with $3H_2O$ in small, brilliant, transparent, elongated prisms, very slightly soluble in cold water, more so in boiling water, insoluble in alcohol. The potassium salt crystallises with $1H_2O$ in spherical masses of slender needles, very soluble in water, and insoluble in boiling absolute alcohol. Both salts become rose-coloured when exposed to light. C. H. B.

Derivatives of Phenylenediamine. By P. Gucci (*Gazzetta*, **23**, i, 295—300; compare Abstr., 1888, 588).—Billeter and Steiner (Abstr., 1887, 366) have prepared orthophenylenethiocarbimide by the action of thionyl chloride on orthophenylenediamine; the author obtained it by heating the latter substance with carbon bisulphide and absolute alcohol in a sealed tube at 100°. It separates from alcoholic solution in iridescent plates melting at 296—297° with slight decomposition. The para-isomeride, first prepared by Lellmann (*Annalen*, **221**, 9) may be obtained by an analogous method.

W. J. P.

Metallic Derivatives of Gallanilide. By P. Cazeneuve (*Compt. rend.*, **117**, 47—50).—When a mixture of gallanilide and sodium hydroxide is dissolved in a very small quantity of hot water, gallanilide separates on cooling, and disodium gallanilide remains in solution, but cannot be crystallised. The liquid gradually blackens in consequence of oxidation. With calcium hydroxide or barium hydroxide solution, gallanilide yields a white precipitate containing only 1 atom of the metal, $NHPh{\cdot}CO{\cdot}C_6H_2(OH){:}O_2M''$. Zinc acetate

in aqueous solution yields the analogous zinc salt as an insoluble, white precipitate; but if this is dissolved in excess of gallanilide, it yields the monobasic salt, which crystallises in yellowish plates. If, on the other hand, zinc acetate in the proper proportion is added to a solution of gallanilide, containing just sufficient ammonia to neutralise the whole of the acetic acid, the tribasic zinc salt is obtained. Lead acetate yields only the bibasic salt; mercuric and cupric acetates give no definite products.

Gallanilide yields insoluble precipitates with alkaloïds, and with aniline it forms the crystallisable compound

$$NHPh\cdot CO\cdot C_6H_2(OH)_3,2NH_2Ph.$$ C. H. B.

Decomposition of Diazobenzene Sulphate in Isoamyl Alcohol. By W. R. Orndorff and C. G. Hopkins (*Amer. Chem. J.*, **15**, 518—523).—The mixture of diazobenzene sulphate and isoamyl alcohol was heated below 100°, using a reflux condenser. The products of the reaction were found to be phenol, isoamyl phenyl ether, benzene, isovaleraldehyde, nitrogen, and sulphuric acid. When metanitrodiazobenzene sulphate was similarly treated, nitrobenzene, isovaleraldehyde, nitrogen, and much metadinitrohydroxyazobenzene, but no metanitrophenol, were found among the products of the decomposition. A. G. B.

Reaction of Alcohols with Paradiazobenzenesulphonic acid. By W. B. Shober (*Amer. Chem. J.*, **15**, 379—391; compare this vol., i, 325).—The alcohols were heated with the acid at different pressures, and the products identified by conversion into amides through the chlorides. The following conclusions as to the course of the reactions are drawn:—(1.) When paradiazobenzenesulphonic acid is decomposed with methyl alcohol under diminished pressure, benzenesulphonic acid alone is produced. (2.) At the ordinary pressure both benzenesulphonic acid and paramethoxybenzenesulphonic acid are formed. (3.) At a *plus* pressure of 350 mm. both products are formed. (4.) At a *plus* pressure of 850 mm. both compounds are formed, but the methoxy-acid predominates. (5.) At a pressure of about 30 atmospheres the methoxy-acid alone is produced. (6.) When ethyl alcohol is used at various pressures up to 850 mm., benzenesulphonic acid alone is produced. (7.) When propyl alcohol is used under the same conditions, benzenesulphonic acid only is formed.

Paramethoxybenzenesulphonamide crystallises in long, slender needles, melts at 113°, and is soluble in hot water and in alcohol; when attacked by fuming nitric acid, it is converted into metadinitrobenzene.

For the preparation of anisoïl the author recommends that diazobenzene nitrate and methyl alcohol be heated together until the temperature rises to 45°. Anisoïl is converted into anisoïldisulphonic acid by the action of ordinary concentrated sulphuric acid.

A. G. B.

Action of Phenylhydrazine on Ethylene Chlorhydrin. By U. Alvisi (*Gazzetta*, **23**, i, 529—535; compare Abstr., 1892, 884).—On boiling a benzene solution of ethylene chlorhydrin with phenyl-

hydrazine, the hydrochloride of the latter is deposited and nitrogen is evolved; salts of ammonium, aniline, and glyoxaldiphenylhydrazine remain in solution. W. J. P.

Constitution of Colouring Matters of the Rosaniline Group. By PRUD'HOMME and C. RABAUT (*Compt. rend.*, **117**, 40—42).—When a current of dry ammonia gas is passed over finely-powdered rosaniline hydrochloride, previously dried at 100° in a vacuum, there is development of heat, and the green, lustrous salt is converted into a violet-purple powder which finally becomes pale carmine. The first change corresponds with the absorption of 1 mol., and the final change with the absorption of 2 mols., of ammonia by 1 mol. of the salt. The whole of the absorbed gas is given off on gently heating, and even in the cold in a dry vacuum. Hexamethylrosaniline-violet, when treated in the same way, yields first an indigo-blue, and then a violet-grey product, strictly analogous in composition to the two compounds just described, and the whole of the ammonia is likewise given off in a dry vacuum in the cold. Aniline hydrochloride, under similar conditions, is completely decomposed by the ammonia which it absorbs, and, since the hydrochlorides of the secondary amines are less stable than those of the primary amines, the author regards these results as affording further support to Rosenstiehl's view that the rosanilines are not salts of amines. C. H. B.

Nitroquinol. By K. ELBS (*J. pr. Chem.* [2], **48**, 179—185).—*Nitroquinol* [$NO_2 : (OH)_2 = 2 : 1 : 4$] is prepared by mixing orthonitrophenol (35 grams), sodium hydroxide (50 grams), and ammonium persulphate (50 grams; this vol., ii, 516) in water (1500 grams), intermittently shaking for 1½—2 days, acidifying with sulphuric acid, distilling off the unchanged nitrophenol with steam, and extracting the residue with ether. It crystallises in yellow or red rhombohedral granules or pyramids and melts at 133—134°; it sublimes with difficulty and dissolves best in alcohol and in ether. It forms two series of salts, which are soluble, with the exception of those of lead, copper, and silver; the solutions of the acid salts are brown, those of the normal salts, violet-blue. The *diacetyl* derivative [$NO_2 : (OAc)_2 = 2 : 1 : 4$] crystallises in colourless laminæ or needles, melts at about 86°, and dissolves in hot alcohol, but not in water. The *dibenzoyl* derivative forms colourless needles, melts, but not sharply, at 140—142°, and dissolves best in hot benzene. Other derivatives, already known, were obtained.

The author recommends ammonium persulphate as an oxidising agent which can be applied in acid, alkaline, or neutral solutions, and has the advantage of not yielding a precipitate as a product of its reduction. A. G. B.

Electrolysis of Substituted Organic Acids. By N. A. BUNGE (*J. Russ. Chem. Soc.*, **24**, 690—694).—A solution of monochloracetic acid (sp. gr. 1·250 at 15°) was electrolysed in a cell divided into two compartments by means of a membrane of parchment paper. The positive electrode was a platinum plate dipping into the solution in

one compartment, the negative electrode being mercury which was covered with mercuric oxide and a solution of sodium hydrogen carbonate in the other compartment. The mercuric oxide was introduced in order to prevent the possibility of the reduction of chloracetic acid to acetic acid and hydrogen chloride. The gas from the positive pole contained nothing but carbonic anhydride and chlorine. When an alkali salt was substituted for the free acid, no chlorine was evolved. Trichloracetic acid gave similar results.

Sodium orthochlorobenzoate yielded oxygen only (and traces of carbonic anhydride), the free acid being deposited on the positive pole. No indication was obtained of chlorine or a chloride in the electrolysed solution. Potassium metanitrobenzoate behaved similarly, but with two platinum electrodes in an undivided cell, a portion of the hydrogen from the negative pole went to reduce the acid.

J. W.

Preparation of Orthochloro- and Orthobromo-benzoic acids. By C. GRAEBE (*Annalen*, **276**, 54—57).—Orthochlorobenzoic acid is most advantageously prepared from anthranilic acid by Sandmeyer's method, observing the precautions described by Erdmann (this vol., i, 150). The yield is 90 per cent. of the theoretical. For the preparation of large quantities of orthochlorobenzoic acid, orthotoluidine is converted into orthochlorotoluene according to Erdmann's directions, and the latter oxidised by boiling it with dilute potassium permanganate solution; this method is obviously less convenient than the first, but the materials are cheaper.

Orthobromobenzoic acid is prepared from anthranilic acid in the same manner as the chlorinated acid; its preparation by oxidising orthobromotoluene is not satisfactory.

A. R. L.

Distinction between Isomeric Amidobenzoic acids and other Isomeric Compounds of the Benzene Series. By O. DE CONINCK (*Compt. rend.*, **117**, 118—120).—The isomeric amidobenzoic acids, nitrobenzoic acids, hydroxybenzoic acids, and the dihydric phenols can be distinguished by the behaviour of their alcoholic or ethereal solutions when exposed to light.

Amidobenzoic acids.—When the dry, solid acids are exposed to light, they undergo no change. In alcoholic solution the ortho-acid shows immediately a blue fluorescence, which persists throughout the insolation, whilst the liquid becomes reddish-brown; the meta-acid shows only a feeble blue fluorescence, and the liquid is bright red; the para-acid becomes pale yellow and eventually orange-yellow, without any fluorescence. In ethereal solution, the following changes are observed: *ortho-*, orange-red, soon changing to pale yellow; *meta-*, pale yellow, any undissolved acid which is in contact with the ether becoming brownish-red; *para-*, a somewhat thick, yellowish film is deposited, whilst the liquid is almost colourless. In diffused light, *ortho-*, reddish-brown, with formation of a deposit of the same colour on the walls of the tube; *meta-*, pale yellow in solution, whilst the solid acid becomes brownish-red where it is in contact with ether; *para-*, no change.

The solutions of orthamidobenzoic acid in various solvents also

show characteristic behaviour; in acetone, the liquid becomes claret coloured, in methyl alcohol, garnet-red, in chloroform, Solferino-red, in dilute hydrobromic acid, violet or amethyst.

Nitrobenzoic acids in the dry state do not change, but alcoholic solutions behave as follows: *ortho*-, colourless; *meta*-, yellow; *para*-, yellow. In ethereal solution, the changes are: *ortho*-, deep yellow and finally pale red; *meta*-, orange, with slight brown, translucid deposit; *para*-, yellow, with a thick, very adherent, orange-red deposit.

Hydroxybenzoic acids in ether undergo no change even after prolonged exposure, except that the *meta*-compound becomes very slightly yellow. Benzoic acid itself undergoes no change.

Dihydric phenols in ethereal solution behave as follows: resorcinol rapidly becomes yellow, then orange, and afterwards pale yellow, with a slight brownish-yellow deposit; catechol soon becomes deep yellow, then brown, and finally amber, without any deposit; quinol, after a long exposure, becomes only pale yellow and remains limpid.

C. H. B.

Mercuric Salicylates. By H. Lajoux and A. Grandval (*Compt. rend.*, **117**, 44—47).—Normal mercuric salicylate, $(OH\cdot C_6H_4\cdot COO)_2Hg$, is obtained as a white precipitate on the addition of a solution of mercuric chloride to a cold solution of sodium salicylate. It is decomposed by heat and is insoluble in water, but dissolves readily in solutions of sodium chloride, potassium cyanide, and potassium iodide, and has the general properties of mercuric salts. When boiled with water, it is converted into salicylic acid and the basic salicylate $C_6H_4<\overset{COO}{\underset{\quad O}{\quad}}>Hg$, which can also be obtained by adding gradually to a boiling aqueous solution of the acid an equivalent quantity of freshly precipitated mercuric oxide, each successive portion being added when the yellow colour of the preceding portion has disappeared. Basic mercuric salicylate is a white powder, insoluble in water, alcohol, ether, or chloroform. When heated, it splits up into water, carbonic anhydride, phenol, mercury, &c. At a red heat a carbonaceous residue is left. The basic salicylate does not show the usual properties of mercuric salts. When suspended in cold water, it is not attacked by hydrogen sulphide until after many hours, but decomposition is more rapid if the liquid is heated. Alkali sulphides dissolve the basic salicylate completely, but the liquid gradually deposits a lemon-yellow precipitate, which very slowly turns black. The salt is slightly soluble in ammonia, very soluble in solutions of sodium hydroxide, sodium chloride, or potassium iodide, especially on heating, and the excess of salt separates in an amorphous form on cooling. All these solutions contain the unaltered salt. Even sodium hydroxide in hot concentrated solution does not decompose it, and hydrogen sulphide yields with the solution the yellow precipitate of mercuric sulphide and salicylate already mentioned. The solutions when dialysed yield the amorphous salt; they are all precipitated by acids and gradually become turbid when exposed to the air.

Cold concentrated hydrochloric acid acts very slowly on the basic salicylate, but the hot acid decomposes it at once. The dilute acid

dissolves it without change. Potassium cyanide also dissolves it, with formation of mercuric cyanide. C. H. B.

Isoeugenolglycollic acid and Eugenolglycollic acid. By M. Denozza (*Gazzetta*, **32**, i, 553—559).—*Isoeugenolglycollic acid*, $CHMe{:}CH{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH$, is prepared by heating a mixture of eugenolglycollic acid (5 grams) with a solution of potash (5 grams) in absolute alcohol (15 grams) in a reflux apparatus for 24 hours at 100°, evaporating, and precipitating with hydrochloric acid. The conversion into the iso-acid is only partial, and there is some difficulty in separating the two. The purified iso-acid forms stellate groups of crystals, and melts at 116°. Isoeugenolglycollic acid is also obtained by acting on isoeugenol with monochloracetic acid and caustic soda.

Barium isoeugenolglycollate, $(C_{12}H_{13}O_4)_2Ba,2H_2O$, loses its water at 115°. The corresponding *methylic* salt is a white, crystalline substance which melts at 90° and yields the *amide* by treatment with ammonia; the latter melts at 213°. No crystalline methylic salt could be obtained from eugenolglycollic acid.

Nitroisoeugenolglycollic acid, $C_{12}H_{13}O_4{\cdot}NO_2$, is prepared by direct nitration, and forms a yellow powder which, after a time, resinifies.

In the preparation of isoeugenol by Tiemann's method (Abstr., 1892, 45), if the product formed by treating amyl alcohol and eugenol with caustic alkali is acidified before distillation in a current of steam, diisoeugenol is obtained, the yield being somewhat better than if Tiemann's process is followed.

Eugenolcinnamic acid, $C_3H_5{\cdot}C_6H_3(OMe){\cdot}O{\cdot}C(COOH){:}CHPh$, may be prepared by heating a mixture of sodium eugenolglycollate, benzaldehyde, and acetic anhydride at 160° in a reflux apparatus; it forms large, anorthic prisms melting at 142°, is insoluble in water or acetic acid, and sparingly soluble in benzene. The *sodium* salt of this acid is anhydrous and only very sparingly soluble in water. The *barium* salt, $(C_{19}H_{17}O_4)_2Ba,\frac{1}{2}H_2O$, and the *silver* salt were also prepared.

W. J. P.

Triacetyldibromogallic acid and Tribenzoyldibromogallic acid. By A. Bietrix (*Bull. Soc. Chim.* [3], **9**, 115—117).—*Triacetyldibromogallic acid*, $C_6Br_2(OAc)_3{\cdot}COOH$, is prepared by heating dibromogallic acid with acetic chloride; it is amorphous, melts at 94—95°, and gives a rose coloration with baryta water or lime water. The *tribenzoyl derivative*, $C_6Br_2(OBz)_3{\cdot}COOH$, is obtained in a similar manner to the preceding compound, which it closely resembles. It can be purified by dissolving it in ether, and precipitating with water; it melts at 95—96°, and gives a green coloration with ferric chloride. Nachbaur's tetracetylgallic acid and Priwoznik's tetracetyldibromogallic acid, both of which compounds are described in Beilstein's Dictionary, thus appear to have been erroneously analysed and classified.

J. B. T.

Basic Gallate of Bismuth (Dermatol). By H. Causse (*Compt. rend.*, **117**, 232—234).—*Basic bismuth gallate* was obtained by Fischer as a yellow powder, but it may be obtained in crystalline form by precipitating a solution of bismuth nitrate with gallic acid in the

presence of potassium nitrate and acetic acid. It forms small, lemon-yellow crystals, having the composition represented by the formula $C_7H_3O_5Bi,2H_2O$, is unstable towards air and light, and dissolves readily in strong acids. *Bismuth pyrogallol*, $C_6H_3O_3Bi$, obtained by mixing acetic acid solutions of bismuth oxide and pyrogallol, forms similar yellow crystals. To determine whether the gallate is a phenolic compound, triacetylgallic acid was treated with bismuth oxide in acetic acid solution. A white powder of *basic bismuth triacetylgallate*, $C_7H_3Ac_3O_2{\cdot}BiO,H_2O$, was obtained, and was also prepared by another method in dehydrated, colourless crystals. A *double gallate of bismuth and magnesium*, $C_7H_2MgBiO_5$, was also prepared; it forms yellow crystals, unstable towards air and light. In consideration of these facts, the constitutional formula of the basic gallate of bismuth is, probably,

$$OH{\cdot}C_6H_2\begin{cases}-O-\\ -O-\\ CO{\cdot}O\end{cases}Bi_2 + 2H_2O.$$

JN. W.

Action of Caustic Alkalis on Phthalides. By P. GUCCI (*Gazzetta*, **23**, i, 319—322).—On heating dimethylphthalide with soda at about 250°, acetone distils and sodium benzoate remains. Knorr states (*Annalen*, **248**, 59) that on heating dimethylphthalide at 100° with potash, potassium hydroxypropylbenzoate is formed; it would thus seem that, on further heating, this salt breaks up into potassium benzoate and acetone. On heating phthalide itself with soda, hydrogen is evolved, and sodium phthalate remains. W. J. P.

Rotatory Power of Salts of Quinic acid. By S. G. CERKEZ (*Compt. rend.*, **117**, 173—177).—The rotatory power of metallic quinates in aqueous solution has been determined by Hesse (*Annulen*, **176**, 124) and Oudemans (*Rec. Trav. Chim.*, **5**, 169). The present series of determinations refers to metallic and alkylic quinates in alcoholic solution and to quinates of nitrogenous bases in both alcoholic and aqueous solutions. The results are as follows.

	Metallic salts (in 98·5 p. c. alcohol).			
	Li.	Am.	Na.	K.
$[\alpha]_D$	−15·2	−14·7	−13·6	−7·2

	Alkylic salts (in 95 per cent. alcohol).					
	Me.	Et.	Pr$^\alpha$.	Pr$^\beta$.	CH_2Pr^β.	Ph.
$[\alpha]_D$....	−28·6	−26·4	−26·4	−27·6	−26·2	−24·7

	Salts of nitrogenous bases.		
	In water. $[\alpha]_D$.	In 95 p. c. alcohol. $[\alpha]_D$.	In 98·5 p. c. alcohol. $[\alpha]_D$.
Diethylamine ..	−31·8	−12·4	−14·3
Pyridine.....	−30·0	−25·1	−27·1
Aniline	−28·5	−22·9	−27·6
Quinoline	−27·4	−22·3	−22·6

Consideration of these figures shows that the introduction of alkylic radicles and metals diminishes the rotatory power to a considerable extent, whilst that of nitrogenous radicles diminishes it to a less extent, except in the case of diethylamine, the rotatory power of the salt of which is nearly the same as that of the metallic salts. Comparing the rotatory powers of the various salts with those calculated by Oudemans' method, on the amount of quinic acid which would be in solution if the dissociations were complete, it is seen that the alkylic, the metallic, and the diethylamine salts are little dissociated in alcoholic solution, whilst those of the other nitrogenous bases are dissociated to a considerable extent. The values calculated from aqueous solutions of the metallic quinates and from those of the nitrogenous bases are not identical, a result confirming that which might be predicted by the electrolytic dissociation theory. Jn. W.

Aldureïdes of Ethylic Acetoacetate and Ethylic Oxalacetate. By P. Biginelli (*Gazzetta*, **23**, i, 360—416; compare Abstr., 1891, 908; 1892, 56).—*Ethylic benzuramidocrotonate*,

$$CO<\begin{matrix}NH—CMe\\NH\cdot CHPh\end{matrix}>C\cdot COOEt,$$

may be prepared by several methods—by heating ethylic acetoacetate or ethylic β-uramidocrotonate with benzaldehyde in alcoholic solution, by boiling an alcoholic solution of ethylic acetoacetate with benzyldiureïde, or by heating ethylic benzalacetoacetate with alcohol and carbamide after acidifying with hydrochloric acid. It forms white laminæ melting at 207—208°, or slender needles melting at 206—206·5°; the latter become slowly converted into the former modification when left in contact with the alcoholic mother liquor. It is slowly hydrolysed by water and dilute acids or alkalis, but, on boiling with potash, it yields benzaldehyde, benzylic alcohol, ammonia, and potassium carbonate in addition to a substance, or mixture, containing nitrogen, which is obtained as a yellow, crystalline powder, blackening at 194—196°. On heating the crotonate with concentrated alcoholic potash, a small quantity of acicular crystals, melting at 150—151°, is obtained; the salt is not acted on by nitrous acid.

Ethylic benzuramidobutyrate, $CO<\begin{matrix}NH\cdot CHMe\\NH\cdot CHPh\end{matrix}>CH\cdot COOEt$, is obtained by reducing the preceding salt with sodium amalgam in alcoholic solution. It forms small needles, melting at 229—230° with decomposition, and is accompanied by a substance obtained as a glassy mass, melting at 59—60°; this is probably a mixture of the compound melting at 229—230° with an isomeride.

A mixture of metanitrobenzaldehyde, ethylic acetoacetate, and carbamide, when heated in alcoholic solution, yields metanitrobenzylidenediureïde and ethylic metanitrobenzalacetoacetate, together with *metanitrobenzylideneureïde*, $CO<\begin{matrix}NH\\NH\end{matrix}>CH\cdot C_6H_4\cdot NO_2$; the latter separates from alcohol as an oil, and is ultimately obtained as a straw-

yellow powder, which melts at about 170°. The mother liquor, on concentration, yields *ethylic metanitrobenzuramidocrotonate*,

$$CO<\begin{matrix}NH\cdot CMe{:}C\cdot COOEt\\ NH\text{——}CH\cdot C_6H_4\cdot NO_2\end{matrix},$$

which crystallises in beautiful, yellow, monosymmetric prisms, $a : b : c = 0{\cdot}729 : 1 : 0{\cdot}1629$; $\beta = 84° 7\frac{1}{2}'$, melting at 231—232°. It is not attacked by ammonium sulphide in hot alcoholic solution.

Cuminaldiureïde, $C_8H_2MePr^a(NH\cdot CO\cdot NH_2)_2$, is obtained by heating a dilute alcoholic solution of cuminaldehyde and carbamide; it is a white, crystalline powder, melts at 175—176°, and is sparingly soluble in ether. On treatment with ethylic acetoacetate, it yields *ethylic cuminaluramidocrotonate*, $C_{17}H_{22}N_2O$, which crystallises in small, colourless needles, and melts at 161—162°; if left in contact with the alcoholic mother liquor for a few days, they change to monosymmetric prisms, $a : b : c = 1{\cdot}3514 : 1 : 1{\cdot}4265$; $\beta = 89° 24'$, which melt at 164—165°; the rise in melting point is also brought about by fusion.

Ethylic salicyluramidocrotonate, $C_{14}H_{16}N_2O_4$, prepared in a similar manner to the analogous compounds described above, crystallises in white needles melting at 199—200°, or in a more stable form as monosymmetric prisms, $a : b : c = 1{\cdot}332 : 1 : 1{\cdot}075$; $\beta = 56° 55'$, which melt at 203—204°. On passing a current of carbonic anhydride through its solution in alcoholic alkalis, and subsequently adding hydrochloric acid, a substance which seems to have the constitution $CO<\begin{matrix}NH\cdot CHMe\cdot CH\cdot O\\ NH\text{——}CH\cdot C_6H_4\end{matrix}$ separates; it forms lustrous laminæ, which decompose at 285°. When heated with dilute sulphuric acid, it yields salicylaldehyde.

Bromine acts on ethylic benzuramidocrotonate in carbon bisulphide solution, yielding a *dibromo*-derivative, $C_{14}H_{16}Br_2N_2O_3$(?), which forms yellow prisms, decomposing at about 173°; it evolves hydrogen bromide continuously, and hence does not give satisfactory numbers on analysis. Under similar conditions, ethylic salicyluramidocrotonate tends to form a dibromo-derivative; on treating it with water, however, hydrogen bromide is given off, and a *monobromo*-derivative, $C_{11}H_{11}BrN_2O_3$, is obtained in colourless needles melting at 192—193°.

The action of carbamide on cinnamaldehyde results in the formation of the following compounds, either of which may become the principal product of the reaction if the conditions be varied. *Cinnamaldiureïde*, $CHPh{:}CH\cdot CH(NH\cdot CO\cdot NH_2)_2$, is obtained as a white, crystalline powder, melting at 171—172°, with decomposition.

Tricinnamaltetraureïde, $C_9H_6(NH\cdot CO\cdot NH\cdot C_9H_8\cdot NH\cdot CO\cdot NH_2)_2$, forms a crystalline powder melting at 182—184° with decomposition. Both the above substances yield cinnamaldehyde and carbamide on boiling with water, alcohol, or acids.

Cinnamalureïde, $CO<\begin{matrix}NH\\ NH\end{matrix}>NH\cdot CH{:}CHPh$, is obtained as a porcelain-like mass, melting at about 115—116°. It behaves similarly to the two ureïdes described above, but absorbs bromine, which they

do not, and, on boiling with alcohol, yields tricinnamaltetraureïde. In addition to the above, a *ureïde*, melting at 212°, and a substance crystallising in small needles melting at 220°, are obtained in the reaction between carbamide and cinnamaldehyde.

Ethylic cinnamaluramidocrotonate, $CO<\begin{matrix}NH\cdot CMe:C\cdot COOEt\\ NH\text{——}CH\cdot CH:CHPh\end{matrix}$, is prepared by boiling either of the cinnamalureïdes with ethylic acetoacetate or, more directly, by heating carbamide, cinnamaldehyde, and ethylic acetoacetate in alcoholic solution. It is obtained as thin, white needles, melting at 243—244°, and absorbs bromine; the compounds thus obtained, however, could not be isolated.

Ethylic benzylidenedihydrocollidinedicarboxylate,

$$NH<\begin{matrix}CMe:C(COOEt)\\ CMe:C(COOEt)\end{matrix}>CH\cdot CH:CHPh,$$

is obtained, together with the preceding compound, on boiling tricinnamaltetraureïde with ethylic acetoacetate and a little alcohol; it forms yellow, transparent, monosymmetric prisms, $a:b:c = 1{\cdot}9270:1:2{\cdot}5607$; $\beta = 72°\ 39'$, which melt at 151—152°. It seems to be isomeric with a substance described by Epstein (*Annalen*, **231**). On treatment with nitrogen trioxide in alcoholic solution, then saturating with carbonic anhydride, and adding hydrochloric acid, a *benzylidenecollidinedicarboxylic acid hydrochloride* is obtained in needles, which decompose at about 120°. This substance gives off hydrogen chloride on exposure to the air, and, on heating with water, yields an *acid*, which crystallises in prisms melting at 156°; the acid obtained by Epstein from his hydrochloride melted at 218—219°.

Difurfuraltriureïde, $CO[NH\cdot CH(C_4OH_3)\cdot NH\cdot CO\cdot NH_2]_2$, is obtained by the action of carbamide on furfuraldehyde; it forms a white powder, which melts at 168—169°, and is insoluble in hot alcohol. It is accompanied by a small proportion of another *ureïde*, which melts at 171—172°, and is very soluble in alcohol. On boiling the triureïde with ethylic acetoacetate, it yields ethylic β-uramidocrotonate and *ethylic furfuramidocrotonate*; the latter forms yellowish, anorthic prisms, $a:b = 2{\cdot}096:1$; $\alpha = 76°\ 9'$, $\beta = 80°\ 41'$, $\gamma = 64°\ 55'$, or leaflets melting at 208—209°.

Ethylic formuramidocrotonate, $CO<\begin{matrix}NH\cdot CMe\\ NH\cdot CH_2\end{matrix}>C\cdot COOEt$, is prepared by heating methenylcarbimide with ethylic acetoacetate dissolved in alcohol; it forms minute needles melting at 260—261°, and is soluble in alcohol.

On heating acetaldehyde, ethylic acetoacetate, and carbamide in alcoholic solution, a substance of the composition $C_{15}H_{22}N_2O_5$ is obtained as a white powder melting at 184°, with decomposition; *ethylic aceturamidocrotonate*, $CO<\begin{matrix}NH\text{—}CMe\\ NH\cdot CHMe\end{matrix}>C\cdot COOEt$, is also formed; this crystallises in anorthic prisms, $a:b:c = 1{\cdot}1561:1:0{\cdot}9112$; $\alpha = 59°\ 5'$, $\beta = 90°\ 51'$, $\gamma = 80°\ 55'$, melts at 195—196°, and is soluble in alcohol.

Ethylic acetylenediuramidocrotonate,

$$CO<\begin{matrix}NH\text{——}CH\text{——————}CH\text{—}NH\\ NH\cdot CMe{:}C\cdot COOEt\quad COOEt\cdot C{:}CMe\cdot NH\end{matrix}>CO,$$

is prepared by heating ethylic acetoacetate, glyoxal, and carbamide in alcoholic solution; it forms white, monosymmetric laminæ, $a : b : c = 2{\cdot}2723 : 1 : 1{\cdot}2020$; $\beta = 75° 42'$, melts at 139°, and is soluble in most organic solvents. It is accompanied by another substance, $(C_3H_2N_2O)_x$, which forms needles melting at 152—154°; this is possibly acetylenedicarbimide, or diacetylenedicarbimide.

Ethylic benzuramidomaleate, $CO<\begin{matrix}NH\cdot C(COOEt)(OH).CH\cdot COOEt\\ NH\text{——————}CHPh\end{matrix}$,

is obtained, together with the following compound, by digesting a mixture of ethylic oxalacetate, benzaldehyde, and carbamide in alcoholic solution; it forms white needles, which melt at 183°, with decomposition. It is not attacked by bromine, but dissolves readily in dilute caustic alkalis, giving an odour of benzaldehyde.

Diethylic benzuramidofumarate, $CO<\begin{matrix}NH\cdot C(COOEt){:}C\cdot COOEt\\ NH\text{————}CHPh\end{matrix}$,

forms white, orthorhombic prisms, showing sphenoidal hemihedrism, $a : b : c = 0{\cdot}8451 : 1 : 0{\cdot}4607$, and melting at 176—177°; it seems to be accompanied by an isomeride which melts at 179°.

Tetrethylic benzodiuramidodimaleate,

$$CHPh<\begin{matrix}NH\cdot CO\cdot NH\cdot C(COOEt)\cdot CH_2\cdot COOEt\\ >O\\ NH\cdot CO\cdot NH\cdot C(COOEt)\cdot CH_2\cdot COOEt\end{matrix},$$

is obtained by treating ethylic benzuramidomaleate with caustic alkali; it separates from its solution in prisms melting at 156—157°, and is very soluble in alcohol.

On adding hydrochloric acid to a solution of either of the three preceding substances in caustic alkali, *ethylic hydrogen benzuramidofumarate*, $C_{14}H_{14}N_2O_6$, is obtained; it forms prismatic crystals which decompose at 220—230°. Its *silver* salt, $C_{14}H_{13}N_2O_6Ag$, melts at 217° with decomposition. *Ethylic methylic benzuramidofumarate* forms white needles which soften at 187°. The ethylic hydrogen salt seems to be accompanied by an isomeride, which is less soluble, and more stable towards heat.

Ethylic hydrogen benzuramidosuccinate, $C_{14}H_{16}N_2O_6$, is prepared by reducing the corresponding fumarate (which decomposes at 220—230°) with sodium amalgam; it crystallises in needles, melts at 224—225°, is not acted on by bromine, and is reprecipitated by hydrochloric acid from its solutions in alkali carbonates.

On heating an alcoholic solution of acetone, carbamide, and benzaldehyde, a white substance, $C_{19}H_{24}N_6O_4$, is obtained, melting at 186—187°; also another compound, $C_{23}H_{30}N_6O_5$, as a white powder melting at 182—183° with decomposition. If a little hydrochloric acid is added to an alcoholic solution of acetone, carbamide, and benzaldehyde, and the mixture kept for two months, a substance which blackens at 280° is obtained, together with a compound of the

composition $C_{27}H_{30}N_6O_4$, which crystallises with alcohol in white needles melting at 270° with decomposition. The latter, on heating with methylic iodide, gives a compound containing iodine, which crystallises in yellow needles decomposing at 220—221°.

Dibenzoacetophenonetetraureïde,

$$CMePh(NH\cdot CO\cdot NH\cdot C_7H_6\cdot NH\cdot CO\cdot NH_2)_2,$$

is obtained by heating an alcoholic solution of acetophenone, benzaldehyde, and carbamide; it is a white powder, which decomposes at 176—180°.

The interaction of benzaldehyde, carbamide, and ethylic ethylacetoacetate yields a *substance* of the composition $C_{26}H_{36}N_6O_6$, which decomposes at 181—183°, and during purification loses benzaldehyde and carbamide, giving a *compound*, $C_{15}H_{18}N_4O_3$, which decomposes at 190—191°. W. J. P.

Heat of Formation of some Derivatives of Indigotin. By R. d'Aladern (*Compt. rend.*, **116**, 1457—1459).—The determinations were made with a calorimetric bomb.

	Heat of combustion.		
	At constant volume.	At constant pressure.	Heat of formation.
Indigotin, $C_{16}H_{10}N_2O_2$....	1815·2	1812·6	+ 41·0 Cal.
Isatin, $C_8H_5NO_2$	867·4	867·8	+ 59·0 „
Isatide, $C_{16}H_{12}N_2O_4$	1777·3	1777·8	+145·0 „
Dioxindole, $C_8H_7NO_3$	915·3	915·7	+ 80·2 „

From these results it follows that

$2C_8H_7NO_2$ sol. + O = $C_{16}H_{12}N_2O_4$ sol. + H_2O liq. ..... develops +53·6 Cal.

and

$C_{16}H_{12}N_2O_4$ sol. + O = $2C_8H_5NO_2$ sol. + H_2O liq. ..... „ +42·0 „

The very considerable development of heat explains the ready oxidation of dioxindole by simple exposure to air. C. H. B.

Acridone. By C. Graebe and K. Lagodzinski (*Annalen*, **276**, 35—53).—The preparation of acridone from phenylanthranilic acid has been already described (Abstr., 1892, 1086). In the present communication, the authors give their experiments in detail, and correct certain misstatements. They were unable to prepare acridone directly from anthranilic acid by a method similar to that employed for the preparation of xanthone from salicylic acid. Pictet and Hubert (*Arch. Sci. phys. nat.*, 1893, 215) have, however, observed that acridone is formed when salicylanilide is strongly heated; they believe that phenylanthranilic acid is an intermediate product.

The preparation of phenylanthranilic acid (*loc. cit.*) is effected from 1 : 3 : 6-amidophenylanthranilic acid, and the compound now employed by the authors as the starting point is orthochlorobenzoic acid, instead of orthobromobenzoic acid. Orthochlorobenzoic acid (this vol., i, 641) is nitrated by boiling it with nitric acid of 1·48 sp. gr., the nitro-acid heated at 170—175° with aniline, and the product reduced with tin and hydrochloric acid. 1 : 3 : 6-*Amidophenylanthranilic acid* is a colourless compound, insoluble in water; it melts at 233—234° with decomposition, yielding chiefly paramidodiphenylamine. The *hydrochloride* crystallises in bright yellow needles, and dissociates when boiled with water; the *stannochloride* also crystallises in yellow needles.

Phenylanthranilic acid is prepared by treating amidophenylanthranilic acid dissolved in alcoholic hydrochloric acid with sodium nitrite at 20—25°, pouring the liquid into a solution of stannous chloride in hydrochloric acid, and precipitating the phenylanthranilic acid with water. The acid decomposes when distilled, yielding principally diphenylamine, but also traces of acridone.

Acridone is prepared as already described (*loc. cit.*); it melts at 354° (corr.), and, like xanthone, forms neither a hydrazone nor an oxime. The methylacridone described by Decker (Abstr., 1892, 881) is obtained by heating a mixture of acridone and potassium hydroxide, moistened with alcohol, at 160—170°, and subsequently heating the pulverised melt with methylic iodide in a sealed tube at 130—140; it melts at 203·5° (corr.), not at 190° (*loc. cit.*). *Ethylacridone*, $C_6H_4<\overset{CO-}{NEt}>C_6H_4$, melts at 159° (corr.). Acridone is readily converted into acridine when it is heated with zinc-dust, treated with sodium amalgam, or fused with potassium cyanide.

Chloracridine, $C_6H_4<\overset{CCl}{N}>C_6H_4$, is obtained by heating acridone at 120—130° with phosphorus pentachloride and some phosphorus oxychloride; it crystallises in colourless needles, melts at 119° (corr.), and sublimes readily; the vapour irritates the mucous membrane, and the compound attacks the skin in the same manner as acridine. On being boiled with water, a portion volatilises, but the greater part is converted into acridone (the latter reaction is exhibited also by its salts), probably through the intermediary formation of the unstable *acridol*, $C_6H_4<\overset{C(OH)}{N}>C_6H_4$. The *hydrochloride* forms long, yellow needles, very soluble in water, and the *picrate* is sparingly soluble in water, and melts above 330°.

To settle the nature of the product which Graebe and Caro obtained (Abstr., 1880, 399) by oxidising acridine, this substance was gently boiled with sodium dichromate and glacial acetic acid; it is found that acridone is first formed, and on continuing the oxidation it is converted into *biacridonyl*, $CO<\overset{C_6H_4}{C_6H_4}>N\cdot N<\overset{C_6H_4}{C_6H_4}>CO$, together with acridinic acid. *Biacridonyl* is also obtained by oxidising ready-formed acridone; it melts at 251°, and, unlike acridone, its solutions

do not exhibit fluorescence, and it is insoluble in alcoholic alkalis. On being heated with zinc-dust, acridine is formed, and hydracrydine is obtained when it is warmed with sodium amalgam. In support of the above constitutional formula, it is urged that methylacridone, when it is oxidised as above, is only with difficulty converted into biacridonyl. A. R. L.

Dichloronaphthalene. By H. ERDMANN (*Annalen*, **275**, 255—261).—1 : 3′-Dichloronaphthalene melts at 48°, the 1 : 2′-isomeride at 62·5°, and the 1 : 3- at 61°; the former is readily characterised by its melting point, whilst the other two are distinguished from each other by their nitration products. The 1 : 2′-compound gives a *mononitro*-derivative melting at 138—139°, whilst the 1 : 3-isomeride under similar conditions yields a *dinitro*-derivative melting at 240°. W. J. P.

Separation and Constitution of Isomeric Naphthalene Derivatives. By H. ERDMANN (*Annalen*, **275**, 184—191).—The author comments on the difficulty of separating isomeric naphthalene derivatives; a direct separation of neutral isomerides is, as a rule, impossible; recourse must be had to the strongly acid sulphonic derivatives. The salts of the sulphonic acids may often be separated with ease by the use of methyl and ethyl alcohols as solvents. In addition to the well-known prefixes, ortho, meta, para, and peri, the author introduces several others, which he thinks will facilitate the description of the isomeric di-derivatives of naphthalene, thus:—*ana* = 1 : 4′; *epi* = 1 : 3′; *kata* = 1 : 2′; *amphi* = 2 : 3′; *pros* = 2 : 2′.

As the double bonds in the naphthalene symbol can be arranged in three different ways, the author considers it possible that three geometrical isomerides of the $\alpha\beta$-heteronucleal di-derivatives of naphthalene may exist; it is, in his opinion, significant that the 1 : 2′-naphthylaminesulphonic acid may be obtained in three forms, containing different quantities of water of crystallisation. W. J. P.

Isomeric α-Mononitronaphthalenemonosulphonic acids. By H. ERDMANN and C. SÜVERN (*Annalen*, **275**, 230—254).—By the nitration of α-naphthalenesulphonic chloride below 3°, a mixture of 1 : 4′- and 1 : 1′-nitronaphthalenesulphonic chlorides is obtained; the product is poured on to ice, washed, and dried. The 1 : 4′-sulphonic chloride is separated from the mass by extraction with boiling carbon bisulphide in a specially devised apparatus, whilst the 1 : 1′-isomeride remains undissolved, and is purified by crystallisation from chloroform.

1 : 1′-*Nitronaphthalenesulphonic chloride* forms fine, colourless prisms, which decompose with evolution of gas at 161°; it is sparingly soluble in ether, light petroleum, or carbon bisulphide, but dissolves readily in most other organic solvents. It is easily hydrolysed by heating with aqueous bases, but does not yield the acid in a pure state when heated with water in a sealed tube. The *sulphonic acid* is obtained by heating its methyl salt with water at 130°; it is readily soluble in water, and separates from the solution in brilliant, yellow needles containing $3H_2O$, of which it retains $1\frac{1}{2}$ at 100°, and $\frac{1}{2}$ in a vacuum

over sulphuric acid. It cannot be obtained anhydrous, and is soluble in alcohol and ether; on reduction, it yields the corresponding amido-acid (Abstr., 1889, 156). The *potassium* salt forms yellow plates, containing $2\frac{1}{2}H_2O$, or asbestos-like needles with $1H_2O$. The *ammonium* salt with $2H_2O$ forms brown, hard plates, and explodes at 210°. The *calcium* salt crystallises with $4\frac{1}{2}H_2O$ in brilliant, yellow plates, and is soluble in water or alcohol, but insoluble in ether; the *barium* salt with $2\frac{1}{2}H_2O$, and the *zinc* salt with $9H_2O$, form hard, brown prisms. The *silver* salt is unstable, separates from its aqueous solution in yellow, anhydrous needles, and is soluble in alcohol. The *sulphonamide* forms white, monosymmetric prisms melting at 185°; it is soluble in chloroform, methyl alcohol, acetone, and acetic acid. The *anilide* is obtained in colourless needles melting at 173°. The *methylic* salt is prepared by heating the sulphonic chloride with methyl alcohol and sodium methoxide; it forms transparent prisms melting at 124°. It is soluble in benzene, and in warm methyl or ethyl alcohol, but only sparingly in chloroform. It is only slowly hydrolysed by heating with water. The *ethylic* salt is prepared by an analogous process, and forms colourless prisms melting at 118°; it is soluble in chloroform.

With the exception of one or two unimportant details, the authors confirm Cleve's description of the 1 : 4′-nitronaphthalenesulphonic acid and its derivatives; the *methyl* salt melts at 117·5°.

A *dinitronaphthalenesulphonic chloride* is also separated from the product of nitrating α-naphthalenesulphonic chloride; it forms large, transparent prisms, which decompose at 117° on rapid heating.

The nitration of β-naphthalenesulphonic chloride yields 1 : 2′- and 1 : 3′-α-nitronaphthalenesulphonic chlorides. W. J. P.

Perinitronaphthalenesulphinic acid. By H. Erdmann and C. Süvern (*Annalen*, **275**, 305—309; compare Limpricht, Abstr., 1892, 475).—On heating perinitronaphthalenesulphonic chloride with a solution of potassium hydrogen sulphite and carbonate, perinitronaphthalenesulphinic acid, $NO_2{\cdot}C_{10}H_6{\cdot}SO_2H$, is formed. Its *paratoluidine* salt forms minute, yellow needles; the *barium* salt separates in small, brilliant scales containing $6H_2O$, whilst the *potassium* salt forms yellow scales with $2H_2O$. On distilling the salts with sulphuric acid in a current of steam, α-nitronaphthalene passes over. W. J. P.

Derivatives of 3′ : 1-Acetonaphthol. By H. Erdmann and F. Henke (*Annalen*, **275**, 291—296; compare Abstr., 1890, 375).—Pure 3′ : 1-acetonaphthol is best obtained by heating its oxime with hydrochloric acid; it melts at 173—174°. On heating it with benzaldehyde and caustic soda, it yields *benzalacetosodionaphthol*, $CHPh{:}CH{\cdot}CO{\cdot}C_{10}H_6{\cdot}ONa$, which crystallises in dark prisms containing $5H_2O$, and absorbs carbonic anhydride from the air. It is very unstable, and, on passing carbonic anhydride through its aqueous solution, *benzalacetonaphthol* is deposited as a yellow, amorphous powder, which readily decomposes, giving benzaldehyde.

Acetonaphthol yields a *monobromo*-derivative in beautiful needles melting at 149°, and a *dibromo*-derivative melting at 124—125°; a

pentabromo-derivative is also obtained in yellow flocks, soluble in carbon bisulphide, benzene, alcohol, or chloroform.

The ethoxy-derivative of acetonaphthol gives a *pentabromo*-derivative, $C_{14}H_7Br_5O_3$; it forms large, colourless prisms melting at 110—111·5°. Acetonaphthol readily gives *dinitracetonaphthol* in brilliant, yellow scales which melt at 145—146° with decomposition.

W. J. P.

Compounds of Substituted Naphthalenesulphonic acids with Organic Bases. By H. Erdmann and C. Süvern (*Annalen*, 275, 297—305).—The salts of the substituted naphthalenesulphonic acids with organic bases are mostly sparingly soluble, stable compounds, and are hence applicable to the isolation of readily soluble sulphonic acids. The authors have examined a number of these salts.

W. J. P.

Synthetical Tri-derivatives of Naphthalene. By H. Erdmann and E. Schwechten (*Annalen*, **275**, 283—291; compare Abstr., 1891, 448).—On heating orthoparadichlorophenylparaconic acid, it loses carbonic anhydride, giving the corresponding isocrotonic acid; on further heating, water distils off, carrying with it 2′ : 4′ : 1-*dichloronaphthol*. This substance forms large, yellow prisms melting at 132°, is soluble in carbon bisulphide or hot water, and gives naphthalene on distillation with zinc dust. Its *monacetyl* derivative melts at 110°. On heating the dichloronaphthol with aqueous ammonia at 150—200°, 2′ : 4′ : 1-*dichloronaphthylamine* is obtained; it crystallises in microscopic needles melting at 116—117°. The *hydrochloride* forms white crystals melting at 204—205°, and is decomposed by water.

Paradichlorophenylparaconic acid gives only a small yield of 1′ : 4′ : 1-*dichloronaphthol* when distilled; the latter melts at 114—115°, and is sparingly soluble in hot water. Its *monacetyl* derivative crystallises in large, yellow prisms which melt at 144—145°. The naphthol is converted into 1′ : 4′ : 1-*dichloronaphthylamine* by heating it with aqueous ammonia at 300°; this base crystallises in white scales, melts at 68—69°, and gives a *hydrochloride* which decomposes at 230°.

On heating, 3 : 4 : 1-dichlorophenylisocrotonic acid yields two isomeric *dichloronaphthols*, which can be separated by means of light petroleum. One of these melts at 149—150°, and gives a *monacetyl* derivative crystallising in white needles and melting at 102—103°; on oxidation with chromic mixture, it yields a *dichlorophthalic acid*, which crystallises in small, white needles containing $1H_2O$, and melts at 189—190°. The other dichloronaphthol forms microscopic needles melting at 83—84°, and gives a *monacetyl* derivative which crystallises in small, white needles melting at 71—72°. W. J. P.

Sulphonation of α-Naphthylamine. By H. Erdmann (*Annalen*, 275, 192—224).—The author disputes the validity of Armstrong and Wynne's explanation (Proc., 1889, 5) of the mixture of isomerides obtained during the sulphonation of, say, α-naphthylamine, on the basis of isomeric change; on sulphonation at 130°, naphthionic acid is the first product, but as time goes on the melt becomes richer and richer in the isomeric 1 : 4′- and 1 : 3′-acids.

Naphthionic acid in contact with hot sulphuric acid readily gives α-naphthylamine; the 1 : 4′-acid decomposes with much less readiness, whilst the 1 : 3′-acid is very stable under such conditions. By continued decomposition of the sulphonic acids at different rates and simultaneous re-sulphonation of the α-naphthylamine, the proportion of the more stable 1 : 4′- and 1 : 3′-acids would continually increase; that α-naphthylamine is always present is shown by the fact that a portion of the melt taken when it is completely soluble in alkali always yields the amine on extraction with ether. The quantity of free α-naphthylamine increases with the time of heating owing to the formation of Dahl's disulphonic acid III. The explanation given above is supported by the results of a series of experiments on the speed of hydrolysis of the various sulphonic acids.

α-Naphthylamine (400 grams), on sulphonation at 125—130° for 22 hours with 95—96 per cent. sulphuric acid (2 kilos.), and subsequent conversion of the product into calcium salt, yields a mixture of calcium 1 : 4′-naphthylaminesulphonate (140—160 grams) and calcium 1 : 3′-naphthylaminesulphonate. The salt of the 1 : 4′-acid is partially separated by crystallisation, and the residue obtained on evaporating the mother liquor to dryness is completely freed from this salt by extraction with absolute alcohol. The salt of the disulphonic acid is then removed by extraction with cold methyl alcohol; the residue, when dissolved in water and acidified, yields the 1 : 3′-acid (55 grams). The calcium salt of the 1 : 4′-acid thus obtained contains a little calcium naphthionate, which may be removed by taking advantage of the fact that the sodium salt of the former acid is soluble in absolute alcohol, whilst sodium naphthionate is only very sparingly soluble.

1 : 3′-Naphthylaminesulphonic acid separates, on acidifying its hot alkaline solution, in white needles changing to compact, brilliant, anhydrous cubes; cooler solutions yield the acid in large, thin leaves containing $2H_2O$. Dilute solutions give a brilliant blue coloration with ferric chloride, and a violet with gold chloride; the acid is sparingly soluble in water. The *sodium* salt forms crystalline crusts containing $1H_2O$; it is soluble in cold methyl alcohol, but only very sparingly so in hot ethyl alcohol. The *potassium* salt, with $1H_2O$, is obtained in large, white crystals, soluble in water, but insoluble in alcohol. The *calcium* salt crystallises in rhomboïdal plates with $7H_2O$ or in small crystals with $2H_2O$; it dissolves readily in water, but is almost insoluble in methyl or ethyl alcohol. The *magnesium* and *zinc* salts form large, rhomboïdal tables containing $12H_2O$; the *cadmium* salt crystallises with $4H_2O$ in small rhombohedra, or in needles containing $8H_2O$. The *silver* salt forms well-defined prisms. 1 : 3′-*Diazonaphthalenesulphonic acid* is obtained by diazotising the potassium salt described above; it forms small crystals which decompose at 94°. On heating it with a mixture of phosphorus tri- and penta-chlorides, it yields the 1 : 3′-dichloronaphthalene; the constitution of the acid is thus determined.

The small proportion of disulphonic acids produced in the sulphonation consists principally of Dahl's α-naphthylaminedisulphonic acid III. The *potassium* salt, $NH_2{\cdot}C_{10}H_5(SO_3K)_2{,}2\frac{1}{2}H_2O$, forms large,

augite-like crystals, and is sparingly soluble in water. The author's experiments indicate that Dahl's α-naphthylaminedisulphonic acid I has no existence.

On sulphonating α-naphthylamine in large quantities for technical purposes, a very small proportion of the so-called ν-naphthylaminesulphonic acid is obtained. The *calcium* salt with $10H_2O$ is soluble in methyl alcohol and water, but is distinguished from the corresponding salt of the 1 : 4′-acid by its very sparing solubility in ethyl alcohol. The free acid forms silky needles, and yields a sparingly soluble *diazo*-compound which gives a bluish-red colour with α-naphthol in alkaline solution. This acid is not obtained in the sulphonation of pure α-naphthylamine. The mother liquor, after separating the calcium salt of this acid, contains a small quantity of the salt of a very sparingly soluble *disulphonic acid;* this is probably derived from β-naphthylamine, and is provisionally termed the ξ-acid. Its *calcium* salt with $5H_2O$ forms slightly coloured needles, is very soluble in water or methyl alcohol, but insoluble in ethyl alcohol. Its aqueous solution is at first unaltered by the addition of ferric chloride, but after a few minutes it acquires a chocolate colour and the solution becomes turbid. With β-naphthol, the *diazo*-compound of this acid gives a bluish-red colouring matter which may be salted out. W. J. P.

Synopsis of the Naphthylaminesulphonic acids. By H. Erdmann (*Annalen*, **275**, 262—282).—The author gives the physical properties, such as solubility, electrical conductivity (Ebersbach, this vol., ii, 451), and heat of combustion, of the seven known naphthylaminesulphonic acids; he has also prepared and examined a number of new salts of these acids. W. J. P.

Behaviour of Sodium or Potassium Naphthionate at High Temperatures. By H. Erdmann (*Annalen*, **275**, 225—230).—Landshoff and Meyer have shown (D. R. Patent, 1890, 56563) that the readily soluble 1 : 2-α-naphthylaminesulphonic acid is formed on heating salts of naphthionic acid at 200—205°. The change from one isomeride to the other is, however, not direct, but decomposition, succeeded by re-sulphonation, occurs. On heating dry sodium naphthionate at 180—220° in a loosely-covered vessel, ammonia, sulphurous anhydride, α-naphthylamine, and a small proportion of volatile colouring matter, soluble in alcohol, are given off, and carbonisation occurs; the residue contains potassium sulphate and salts of disulphonic acids, of the 1 : 2-monosulphonic acid, and of naphthionic acid.

Cleve's statement (Abstr., 1892, 345) that the 1 : 2-acid crystallises with $\frac{1}{2}H_2O$ seems to be erroneous; a little water is merely carried down mechanically during separation. The aqueous solution of this acid gives a green precipitate with ferric chloride, and reduces gold chloride. W. J. P.

Mixed Naphthylazo-compounds. By G. Oddo and G. Ampola (*Gazzetta*, **23**, i, 257—263).—*β-Naphthylazonitroethane*, $C_{10}H_7{\cdot}N{:}N{\cdot}CHMe{\cdot}NO_2$,

separates in voluminous, yellow flocks on slowly mixing ice-cold solutions of β-diazonaphthalene chloride and sodionitroethane; it is purified by dissolving in caustic potash and precipitating by hydrochloric acid. It forms lustrous, red scales which melt at 145° with rapid decomposition; it is soluble in alcohol, but only sparingly so in chloroform, benzene, ether, or light petroleum, and has a strawberry-like odour.

β-Naphthylazonitrosonitroethane, $C_{10}H_7{\cdot}N_2{\cdot}CMe(NO){\cdot}NO_2$, is precipitated on adding hydrochloric acid to a caustic potash solution of the previous compound, to which potassium nitrite has been added; it forms dark red needles melting at 141°, and gives Liebermann's reaction for nitroso-compounds.

β-Naphthylazobromonitroethane, $C_{10}H_7{\cdot}N_2{\cdot}CMeBr{\cdot}NO_2$, is obtained by direct bromination in alcoholic solution, and crystallises in yellow scales or needles which melt at 168° with decomposition; it is insoluble in alkalis.

α-Naphthylazonitroethane is obtained in a similar manner to the β-isomeride; the yield is, however, much smaller. It forms dark red scales melting at 105·5—106°.

The action of various reducing agents on the β-isomeride was investigated in the hope of obtaining the hitherto unknown ethilidenediamine; the only products isolated, however, were ammonia and β-naphthylamine. W. J. P.

Oxygenated Derivatives of Acenaphthene. By C. Graebe and E. Gfeller (*Annalen*, **276**, 1—20; compare Abstr., 1892, 863).—The so-called acenaphthenequinone (*loc. cit.*) is best prepared by stirring pulverised sodium dichromate (40—45 grams), not too slowly, into a mixture of acenaphthene (10 grams) and glacial acetic acid (70 c.c.) at a temperature of 100°, precipitating with water, and extracting the crude compound with a boiling 40 per cent. solution of sodium hydrogen sulphite. Under these circumstances, the additive *compound*, $C_{12}H_6O_2,NaHSO_3 + 2H_2O$, is formed, and when cold sulphuric or hydrochloric acid is added to its aqueous solution, acenaphthenequinone is precipitated. Acenaphthenequinone, like phenanthraquinone, exhibits Laubenheimer's reaction, thus:—When the finely pulverised compound is suspended in glacial acetic acid, (1) on addition of crude toluene and an excess of concentrated sulphuric acid, a dirty green liquid is formed which, when shaken with ether, colours the latter a deep red; (2) on the addition of concentrated sulphuric acid and a drop of thiophen, a dark green liquid is obtained which, when shaken with chloroform, colours it blue or bluish-violet.

When acenaphthenequinone is heated at 100° in a sealed tube with concentrated ammonia, a red *compound* is obtained which does not melt at 300°, and has, probably, the constitution $(C\langle{}^{N}_{C_{10}H_6}\rangle C)_2O$.

The *dioxime*, $C_{10}H_6\langle{}^{C{\cdot}NOH}_{C{\cdot}NOH}$, is a colourless compound melting at

222° with decomposition; the *hydrazone*, $C_{10}H_6<\begin{matrix}CO\\|\\C{:}N_2HPh\end{matrix}$, crystallises in small, orange needles, and melts at 179°; whilst the *dihydrazone*, $C_{10}H_6<\begin{matrix}C{:}N_2HPh\\|\\C{:}N_2HPh\end{matrix}$, formed by heating the quinone with an excess of phenylhydrazine at 130—140°, crystallises in small, dark yellow needles, and melts at 219°. The authors have qualitatively established that acenaphthenequinone behaves with orthodiamines and with ethylic acetoacetate in a manner similar to phenanthraquinone. Acenaphthenequinone is quantitatively converted into naphthalic acid by warming it with sodium or potassium dichromate and glacial acetic acid or sulphuric acid. It is less readily reduced than phenanthraquinone, and a dihydroxy-derivative (quinol) was not isolated. Sulphurous acid only attacks it at 150°, and biacenaphthylidenediketone (see below) is formed. When the quinone is heated with zinc-dust and acetic acid, various products are obtained, and among them acenaphthenone and acenaphthene.

Acenaphthenone, $C_{10}H_6<\begin{matrix}CH_2\\|\\CO\end{matrix}$, is prepared by adding zinc-dust, in small portions at a time, to a boiling solution of acenaphthenequinone in glacial acetic acid until it is decolorised. It forms colourless leaflets melting at 121°. It dissolves in alcoholic potash, forming a violet solution from which it is reprecipitated unchanged on acidification, but when boiled with sodium hydroxide it is converted into naphthalic acid. The *oxime*, $C_{10}H_6<\begin{matrix}CH_2\\|\\C{:}NOH\end{matrix}$, forms colourless leaflets, and melts at 175°.

Naphthaldehydic acid (*loc. cit.*) melts at 167—168° (not 172°), and on raising the temperature higher it resolidifies, and melts a second time at 290—295°; the *calcium* salt, $(C_{12}H_7O_3)_2Ca$, is readily soluble in water. Neither the acid nor its salts give a coloration with a magenta solution decolorised by sulphurous acid. Alkaline potassium permanganate converts naphthaldehydic acid into naphthalic acid, whilst nitric acid, or glacial acetic acid and chromates, converts it into naphthalic anhydride. The *acetyl* derivative, $C_{10}H_6<\begin{matrix}CH(OAc)\\CO\end{matrix}\!\!\!

obtained by the incomplete oxidation of acenaphthene with glacial acetic acid and a chromate, and also by heating acenaphthenequinone with dilute hydriodic acid and red phosphorus in a sealed tube at 115—125°; it melts at 295° (corr.). The diketone is not attacked by alkalis; but concentrated sulphuric acid dissolves it with a green colour which changes to red on adding a drop of nitric acid. If the diketone is heated with hydriodic acid and phosphorus at 160—170°, a carbonaceous mass is formed from which a small quantity of acenaphthene may be isolated. The *dibromide*, $C_{24}H_{18}Br_2O_2$, melts at 237°, and the *hydrazone*, $C_{30}H_{18}N_2O$, forms a brownish-red, crystalline powder, and melts at 105—110°. A. R. L.

Phenanthridone. By C. Graebe and C. A. Wander (*Annalen*, **276**, 245—253).—In order to ascertain whether the so-called hydroxyphenanthridine obtained by Pictet and Ankersmit (Abstr., 1892, 196) is identical with Graebe and Aubin's phenanthridone (Abstr., 1889, 145), the authors reduced nitrodiphenylcarboxylic acid, and obtained, besides amido-acids, a small quantity of a compound insoluble in alkalis, identical with phenanthridone (m. p. 293°). However, they subsequently examined a specimen of Pictet and Ankersmit's preparation, and found that it did not give a benzyl derivative, as phenanthridone does (see below). They suggest that the so-called hydroxyphenanthridine may have the constitution

$$\begin{matrix} C_6H_4\cdot N & - & N & - & C_6H_4 \\ | & & | & & | \\ C_6H_4\cdot CO & & CO\cdot C_6H_4' & & \end{matrix}$$

analogous to biacridonyl. Phenanthridone is best prepared by treating an alkaline solution of diphenaminic acid, or of diphenamide, with a hypochlorite or hypobromite, and subsequently with sulphurous acid, and finally precipitating the compound with an excess of dilute sulphuric acid. It is insoluble in aqueous alkalis and dilute acids, but dissolves in alcoholic alkalis; its solutions, unlike those of acridone, do not exhibit fluorescence. It does not form an acetyl derivative, remains unaltered when treated with acetic acid and sodium dichromate, and is converted into the potassium derivative when heated at 300° with potassium hydroxide. When phenanthridone is heated with zinc-dust, phenanthridine is formed; the production of the latter from phenanthrene through diphenaminic acid takes place in six stages. *Chlorophenanthridine*, $\begin{matrix} C_6H_4\cdot CCl \\ | \\ C_6H_4\cdot N \end{matrix}$, is obtained by heating phenanthridone in a sealed tube at 190° with phosphorus pentachloride; it forms colourless needles, melts at 116·5° (corr.), is soluble in alcohol, and is converted into phenanthridone when heated with lime.

Methylphenanthridone, $\begin{matrix} C_6H_4\cdot NMe \\ | \\ C_6H_4\cdot CO \end{matrix}$, is obtained by heating the potassium derivative of phenanthridone with methylic iodide in a sealed tube at 150—160°; it melts at 108·5° (corr.). The corresponding *ethyl* derivative melts at 89° (corr.), and the *benzyl* derivative at 112·5° (corr.). The authors contend that the foregoing results favour

the view that phenanthridone is a ketonic, and not a hydroxylic, compound. A. R. L.

Dihydroxyanthraquinoneformamides. By PRUD'HOMME and C. RABAUT (*Bull. Soc. Chim.* [3], **9**, 131—133).—*Dihydroxyanthraquinoneformamide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)_2\cdot NH\cdot CHO$ [OH : OH : NH=1:2:3], is formed on boiling the corresponding dihydroxyamidoanthraquinone with 10 parts of formic acid (70 per cent.), and is a yellow compound giving a violet-blue coloration with alkalis, and a violet-red one with ammonia. It combines with mordants, yielding an orange dye with aluminium, and brown with iron and chromium. On heating with sulphuric acid and glycerol, alizarin-blue is formed, whilst by the action of concentrated alkalis, or of sulphuric acid alone, it is resolved into its constituents. The isomeric formamide [OH : OH : NH = 1 : 2 : 4] is prepared in a similar manner to the preceding compound, which it closely resembles. Towards mordants it behaves like dihydroxyanthraquinone. J. B. T.

Pine Needle Oils. By J. BERTRAM and H. WALBAUM (*Arch. Pharm.*, **231**, 290—305).—A number of samples of pine needle oil have been investigated by the authors, partly to provide data for the detection of sophistication, and partly to determine the various constituents; the latter have been identified both by their physical properties and by the preparation of well-characterised derivatives. The rotatory powers were observed in a 100-mm. tube. The oil from the needles of *Abies pectinata*, D.C., is lævorotatory; the sp. gr. = 0·875 at 15°; the rotatory power = −20° 40′; on distillation under ordinary pressure, 8 per cent. passes over at 150—170°, and 55 per cent. at 170—185°; at higher temperatures, decomposition takes place. The oil consists of lævopinene, lævolimonene, lævobornylic acetate (4·5 per cent.), and sesquiterpene (Wallach's cadinene).

Pine twig oil from *Abies pectinata*, D.C., has been investigated by Wallach; the sp. gr. = 0·854; rotatory power = −72°; on distillation, 16 per cent. passes over at 150—170°, and 76 per cent. at 170—185°. The oil consists of lævopinene, lævolimonene, and bornylic acetate (about 0·5 per cent.).

Spruce oil from *Abies canadensis*, L., consists of lævopinene, lævobornylic acetate (36 per cent.), and cadinene. The sp. gr. = 0·907°; the rotatory power = −20° 54′; 11 per cent. passes over at 150—170°, and 37 per cent. at 170—185°.

The needles and twigs of *Picea vulgaris*, Lk., yield an oil of sp. gr. = 0·888 at 15°; the rotatory power = −21° 40′; 20 per cent. distils at 160—170°, and 50 per cent. at 170—185°; the oil consists of lævopinene, lævophellandrene, dipentene, lævobornylic acetate (8·3 per cent.), and cadinene.

The oil of *Pinus pumilio*, Haenke, has already been investigated by Atterberg (*Ber.*, **14**, 2530); the sp. gr. = 0·865 at 15°; the rotatory power = −9°; 70 per cent. distils at 170—185°; the oil consists of lævopinene, lævophellandrene, silvestrene, bornylic acetate (5 per cent.), cadinene, and probably a little dextropinene.

Swedish pine needle oil from *Pinus silvestris*, L., is dextrorotatory, = +10° 40′; the sp. gr. = 0·872 at 15°; 44 per cent. distils at 160—170°, and 40 per cent. at 170—185°; the oil consists of dextropinene, dextrosilvestrene, and probably bornylic acetate. A sample of oil of the same kind as that just described, but from trees grown in Germany, is also dextrorotatory, = +10°; the sp. gr. = 0·886 at 15°; 10 per cent. distils at 160—170°, and 46 per cent. at 170—185°. The oil is composed of dextropinene, dextrosilvestrene, and cadinene, an acetate which is probably the bornyl salt, and perhaps a little dipentene.

The characteristic odour of pine oils is due to the presence of bornylic acetate. The authors have prepared both modifications synthetically; the lævorotatory compound is identical with the natural product; the dextrorotatory modification only differs in the sign of its rotation. The acetate is deposited from light petroleum in large, hemihedral crystals belonging to the rhombic system; for the dextro-modification $a : b : c = 0{\cdot}69653 : 1 : 0{\cdot}45362$; for the natural lævo-modification $a : b : c = 0{\cdot}69934 : 1 : 0{\cdot}46171$; it melts at 29°, boils at 98°; the sp. gr. = 0·091; the rotatory power = 38° 20′. *Bornylic formate* boils at 90°; the sp. gr. = 1·013; refractive power = +31°. *Bornylic propionate* boils at 109—110°; sp. gr. = 0·979°; refractive power = +24°. *Bornylic butyrate* boils at 120—121°; sp. gr. = 0·966; refractive power = +22°. *Bornylic valerate* boils at 128—130°; sp. gr. = 0·956°; refractive power = +20°. The boiling points of the above salts were observed under a pressure of 10 mm., the sp. gr. at 15°; they resemble the acetate in general properties, but the characteristic odour decreases with increasing molecular weight. J. B. T.

Isonitrosocamphor. By G. Oddo (*Gazzetta*, **23**, i, 300—306; compare Abstr., 1889, 619; 1893, i, 422).—The *ethyl* derivative of isonitrosocamphor, $C_{10}H_{14}O{:}NOEt$, is obtained by digesting a mixture of sodium ethoxide, ethylic iodide, isonitrosocamphor, and alcohol in a reflux apparatus. It forms white, waxy scales melting at 72—73°, and is very soluble in alcohol, ether, benzene, or chloroform, but insoluble in water or cold alkalis; it is almost odourless, and is hydrolysed by alcoholic potash with production of isonitrosocamphor. The *methyl* derivative can be obtained by a similar method, but only in an impure state as a yellow oil. On heating isonitrosocamphor with acetic chloride, a *substance*, $C_{12}H_7NO_2$, is obtained, which forms six-sided prisms melting at 172°, and is not a simple acetyl derivative; it is soluble in alcohol, benzene, or chloroform, but only sparingly in ether. When hydrolysed by alcoholic potash, it does not give isonitrosocamphor, but a *substance* which forms prismatic needles melting at 143—144°. Benzoic chloride acts readily on isonitrosocamphor at 100°; the author has, however, not yet succeeded in obtaining the products in a crystalline state. W. J. P.

The Camphor Group. By U. Alvisi (*Gazzetta*, **23**, i, 332—341; compare Abstr., 1892, 1343).—*β*-Dibromocamphor readily reacts with phenylhydrazine at 100°, yielding a substance of the composition $C_{10}H_{14}(N_2HPh)_2$, which may be purified by reason of its non-volatility in a current of steam; it is a yellow, amorphous powder melting at

68·5°, and is soluble in alcohol, ether, benzene, or acetic acid, but insoluble in water. When boiled with hydrochloric acid, it undergoes partial resinification, and with acetic chloride it yields an *acetyl* derivative, $C_{10}H_{14}(N_2PhAc)_2$, as an amorphous powder. It also gives resinous products on reduction with sodium amalgam, and does not yield a chlorinated hydrocarbon by Baeyer and Zincke's reaction (Abstr., 1892, 842).

Potassium permanganate, in alkaline or acid solution, oxidises β-dibromocamphor with evolution of carbonic anhydride; a syrupy acid is obtained, but no conclusion as to its composition could be derived from analyses of its insoluble lead and barium salts.

Campholenic acid and phenylhydrazine react in the cold yielding *phenylhydrazine campholenate*, $PhN_2H_3,C_{10}H_{16}O_2$; it forms acicular needles melting at 48·5—49·5°, and on heating at 50—100° loses weight and resinifies. The base and acid react violently when heated together, ammonia being evolved. W. J. P.

Dextrogyrate Licareol. By P. Barbier (*Compt. rend.*, **116**, 1459—1461).—Essence of coriander, on fractionation, yields a hydrocarbon, $C_{10}H_{16}$, boiling at 165—180° under the ordinary pressure, an oxidised compound which boils at 120° under a pressure of 16 mm., and which will be described subsequently, and an alcohol, *coriandrol*, boiling at 92—93° under a pressure of 15·5 mm. (Abstr., 1882, 525).

Coriandrol is a colourless liquid, with an odour very different from that of licareol, but in other physical properties the two compounds are practically identical, except that coriandrol is dextrogyrate.

	Coriandrol.	Licareol.
Boiling point	196—198°	198—200°
Sp. gr. at 0°	0·8820	0·8819
Refractive index n_r	1·4641	1·4635
Refractive index n_b	1·4781	1·4775
Rotatory power	+15° 1′	−18° 21′

Coriandrol, like licareol, yields a liquid tetrabromide, and when carefully oxidised, it yields an aldehyde, $C_{10}H_{16}O$, practically identical with licaraldehyde in physical properties. When subjected to the action of strong oxidising agents, coriandrol yields the same products as licareol; the author was unable to confirm Grosser's statement that it yields dimethylsuccinic acid (*loc. cit.*). With hydrogen chloride, it yields a liquid dihydrochloride identical with that obtained from licareol, and when treated with acetic anhydride it yields a limonene which cannot be distinguished from licarene, and at the same time there is formed the acetate of an alcohol which appears to be identical with licarhodol.

It would seem from these results that coriandrol must be regarded as detrogyrate licareol. C. H. B.

Constitution of Rhodinol. By P. Barbier (*Compt. rend.*, **117**, 177—178).—*Rhodinol*, $C_{10}H_{18}O$, a constituent of the liquid portion of

oil of roses, has been shown by Eckart (Abstr., 1892, 203, 625) to be a primary alcohol, yielding valeric acid as one of the products of oxidation, and having a formula containing two ethylene bonds. It is thus an isomeride of licareol (compare this vol., i, 496) and geraniol. Rhodinol is an oily liquid, boiling at 126·5° under a pressure of 16 mm., and having a sp. gr. of 0·8956 at 0°, refractive indices $n = 1·4653$ for λ 645 and $n = 1·4795$ for λ 452·6, and a specific rotatory power $[\alpha]_D = -2° 37'$ at 25°. When treated with gaseous hydrogen chloride, it yields dipentene dihydrochloride, which boils at 147° under a pressure of 18 mm., has a sp. gr. of 1·051 at 0°, and is converted by a boiling acetic acid solution of potassium acetate into dipentene, recognised by its characteristic bromide melting at 124°. The formula deduced from these various reactions is $CH_2{:}CMe{\cdot}CH{:}CH{\cdot}CHPr^{\alpha}{\cdot}CH_2{\cdot}OH$. To determine which of the two possible stereometric formulæ is to be assigned to rhodinol, the latter was heated with acetic anhydride at 180°. The *acetate* thus formed is a colourless, mobile liquid of agreeable odour, boiling at 131° under a pressure of 15 mm., and having a sp. gr. of 0·9214 at 0°, and refractive indices $n = 1·4526$ for λ 645 and $n = 1·4661$ for λ 452·6. When hydrolysed with alcoholic potash, it is reconverted into an alcohol, identical with rhodinol, which is therefore the stable modification. Jn. W.

Bulgarian (Turkish) Oil of Roses. By V. Markovnikoff and A. Reformatsky (*J. Russ. Chem. Soc.*, **24**, 663—686).—The material examined by the authors consisted of three rose oils from different parts of Bulgaria, which liquefied completely at 23·5°, 24°, and 24° respectively, and had the sp. gr. 0·8563, 0·8603, and 0·8639 at 27·5°/0°. At the ordinary temperature, they were thick, yellowish liquids, containing transparent, crystalline plates, and having a strong odour of roses, modified by a slightly fusty smell. They were all optically active, rotating the plane of polarisation about 3·5° to the left in a 100 mm. tube.

In order to effect a separation of the elæoptene and stearoptene contained in it, the oil was cooled to 0° and filtered, the filtrate being cooled to −55°, and refiltered until no more solid separated. The liquid elæoptene obtained in this way, when dried over fused potash, was a yellowish, mobile liquid, the rotation of which in a 100 mm. tube was −3° 44'. On repeated distillation at the ordinary pressure, it yielded as chief fraction a liquid boiling at 222—222·5° (224·7°, corr.), and when freshly distilled had the composition represented by the formula $C_{10}H_{20}O$. This substance was shown to be an alcohol, and the authors have named it *roseol* (roseolic alcohol). Roseol smells of oil of geraniums, but on standing in the air it rapidly oxidises, thereby acquiring the odour of roses. It is a colourless, fairly mobile liquid, with a sp. gr. = 0·87846 at 20°/20° and 0·87498 at 20°/4°. Its molecular refractive power at 20°, according to Lorentz's formula, is $R_a = 49·48$.

Its solution in carbon tetrachloride at once decolorises a solution of bromine in the same solvent, the amount of bromine disappearing being 3 atoms per molecule of roseol. A separate experiment showed

that 2 atoms of bromine are absorbed without evolution of hydrogen bromide.

The acetate, $C_{10}H_{19}\cdot OAc$, formed by heating 9 parts of roseol with 7 of acetic anhydride for 24 hours on a sand bath, boils at 235—236°, and is a colourless, pleasant-smelling liquid.

On oxidation at the ordinary temperature with 1 per cent. potassium permanganate solution, roseol yields no products volatile with steam, but gives a syrup which distils at 240° under 100 mm. pressure. Analysis showed this to be the *glycerol* $C_{10}H_{19}(OH)_3$, a thick, faintly yellow liquid, which does not solidify at −50°. It has a faint odour of roses, and a taste at first sweet, but afterwards burning. Its sp. gr. at 0°/0° is 1·0445, and at 20°/0° 1·0343. It is easily soluble in water, but only slightly in alcohol or ether. Bromine is not decolorised by it, even on long standing. The *triacetate*, $C_{10}H_{19}(OAc)_3$, formed by heating the glycerol at 150° with excess of acetic anhydride, boils at 215—220° under 40 mm. pressure, and solidifies at −10°. It has an aromatic odour, and a sp. gr. = 1·0594 at 0°/0°.

Roseol (5 grams) was dissolved in 10 times its volume of light petroleum, and added drop by drop to phosphoric anhydride (2 grams), covered by the same solvent, and cooled in ice. After remaining for two hours at the ordinary temperature, the light petroleum was poured off, washed with sodium carbonate solution, dried, and distilled on the water bath. The residue, on fractionation, yielded as chief product a liquid boiling at 180—185°, and having the composition $C_{10}H_{18}$. This hydrocarbon is a very mobile and slightly fluorescent liquid, which smells of camphor, and oxidises rapidly in the air. No terpene could be detected in the crude hydrocarbon.

When heated for 12 hours at 180—200° with 40 volumes of hydriodic acid saturated at 0°, roseol gives a saturated hydrocarbon $C_{10}H_{22}$, which boils at 158—159°, has the vapour density 4·91, and sp. gr. = 0·7554 at 20°/0°.

The authors contend that their results prove the chief constituent of the elæoptene of rose oil to be an unsaturated alcohol of the formula $C_{10}H_{20}O$, isomeric with allyldipropylcarbinol (b. p. 192°) and allyldiisopropylcarbinol (b. p. 169—171°). Judging from the high boiling point (220°), it is probably normal. The results obtained by Eckart (Abstr., 1891, 323; 1892, 203, 625), who stated that the chief constituent of Turkish rose oil elæoptene was rhodinol, $C_{10}H_{18}O$, are questioned on the ground that he worked with impure (partially oxidised) material (compare, however, preceding abstract).

The solid *stearoptene* obtained from the original oil by freezing constituted about 20 per cent. of the whole. It was recrystallised several times from 98 per cent. alcohol, in which it is moderately soluble, and dried first over sulphuric acid, afterwards for a short time at 100°. The purified substance melted at 36·5—36·8°, solidified at 34°, and boiled between 350° and 380°; analysis and a molecular weight determination in benzene showed that it is a saturated hydrocarbon of the formula $C_{16}H_{34}$. Small quantities of other hydrocarbons were also found to be present. J. W.

Geraniol. By P. Barbier (*Compt. rend.*, **117**, 120—122).—Essence of *Andropogon schœnanthus*, when fractionated, yields about 75 per cent. of geraniol, mixed with a small quantity of a sesquiterpene, which increases its specific gravity and renders it lævorotatory. When this geraniol is heated with acetic anhydride in a sealed tube at 150°, it yields only the acetate $C_{19}H_{17}\cdot OAc$, a colourless, mobile liquid, which has a pleasant odour, and boils at 129—130° under a pressure of 14·5 mm.; sp. gr. at 0° = 0·9388; refractive index at 24°, $n = 1{\cdot}4614$ for λ 645 and $n = 1{\cdot}4758$ for λ 452·6. When heated with alcoholic potash, this acetate rapidly hydrolyses, and yields pure geraniol, a colourless, slightly oily liquid, with a fine odour; it boils at 126—127° under a pressure of 16 mm.; sp. gr. at 0° = 0·9012; refractive indices at 24°, $n = 1{\cdot}4750$ for λ 645 and $n = 1{\cdot}4904$ for λ 452·6. With hydrogen chloride, it yields a liquid dihydrochloride, boiling at 142—143° under a pressure of 16 mm., and when this is treated with a boiling solution of potassium acetate in acetic acid, it yields dipentene.

The author considers that the product obtained by Bouchardat by the action of acetic anhydride on linalol (this vol., i, 544) is licarhodol and not geraniol, the linalol itself being the unstable stereoisomeride of geraniol. C. H. B.

Santonin. By J. Klein (*Arch. Pharm.*, **231**, 213—234; compare this vol., i, 111 and 363).—The author confirms his previous observation of the production of α-santigendilactone by the reduction of santonin with zinc in acetic acid solution; santonone, $(C_{15}H_{17}O_3)_2$, contrary to the statement of Grassi-Cristaldi (this vol., i, 110), does not appear to be formed. The action of phosphoric chloride on santonin has already been described (this vol., i, 425). Santonin oxime crystallises with $1H_2O$. The acetyl derivative, $C_{15}H_{18}NO_3Ac$, melts at 165—166° or at 169—170° with decomposition, according to the rapidity with which it is heated, instead of at 201—203° as stated by Gucci, and is readily hydrolysed by alcoholic potash or ammonia. The *benzyl derivative*, $C_{15}H_{18}NO_3\cdot C_7H_7$, crystallises in needles melting at 151—152°. The oxime may also be prepared in alkaline solution; on acidification with hydrochloric acid, it gives a violet-red coloration with ferric chloride, which probably points to the existence of a syn-hydroximic acid. On dissolving the oxime in alkali, and subsequently acidifying and adding ferric chloride, a yellow colour is produced, indicating the existence of an "anti-" acid; the "syn-"compound is tolerably stable in solution, but cannot be reconverted into its isomeride.

The paper concludes with a discussion of the constitution of santonin, and a criticism of the work of several Italian chemists on the subject. The author is of opinion that the properties and reactions of santonin can only be explained on the assumption that it is the α-lactone of a hydroxy-α-ketonic acid of the formula

$$\begin{matrix} CH_2\cdot CO \\ | \\ C_{12}H_{16}\cdot O \end{matrix}\!\!>\!CO.$$

J. B. T.

Oxidation Products of the Santononic acids. Diparaxylyl and Diphenyl. By G. GRASSI-CRISTALDI (*Gazzetta*, **23**, i, 306—308).—The author hopes to demonstrate the production of diphenyl and diparaxylyl during the oxidation of the isomeric santononic acids with nitric acid; he has, however, not yet analysed the products of the reaction. W. J. P.

Derivatives of Photosantonic acid. By S. CANNIZZARO and P. GUCCI (*Gazzetta*, **23**, i, 286—294).—On passing a current of dry hydrogen chloride through a solution of photosantonic acid in 90 per cent. alcohol, and distilling off the solvent under reduced pressure, a mixture of dextro- and inactive dehydrophotosantonic acids is obtained; the quantity of the active acid produced decreases as the time of passing hydrogen chloride through the solution increases, and if the solution is boiled during treatment with the gas, only the inactive acid is obtained (compare Abstr., 1886, 73; 1892, 869).

On heating either the active or inactive acid considerably above its melting point, or on distilling it under reduced pressure at 290—300°, a new bibasic isomeride seems to be produced; it forms very hard prisms melting at 133·5—134·5°, and is inactive. All the three acids, when distilled with barium oxide, yield a *hydrocarbon*, $C_{13}H_{20}$. On oxidation with chromic acid mixture, this substance and the three isomeric dihydrophotosantonic acids all give a dimethylphthalidecarboxylic acid, $\begin{matrix} HC\cdot CH{:}C\cdot CMe_2 \\ \| \quad\quad | \\ COOH\cdot C\cdot CH{:}C\text{—}CO \end{matrix}\!>\!O$, which crystallises in long, white needles melting at 205—206°; its *ethylic* salt forms white prisms which melt at 105—106°. On heating in a sealed tube at 180—190° with hydriodic acid, the acid yields a white substance melting at 236—236·5°; this may be reconverted into the acid by oxidising agents. When distilled with baryta at 350°, the acid gives benzene, and, on heating with potash, it yields isophthalic acid.

W. J. P.

Preparation of Pure Digitonin. By H. KILIANI (*Arch. Pharm.*, **231**, 460—461).—The solution in hot 85 per cent. alcohol of the crude substance ("digitalinum pur. pulv.," compare Abstr., 1891, 576) should not be allowed to cool, but should be placed on a water bath at 45°, kept for six hours at this temperature, and then allowed to cool slowly. The glucoside is then deposited in a form in which it is much more easily drained by the pump. C. F. B.

Derivatives of Digitogenin. By H. KILIANI (*Arch. Pharm.*, **231**, 448—460).—The action of various reagents on digitic acid was tried, but no well-characterised products could be obtained. The mother liquors from digitic acid, prepared by oxidising digitogenic acid with alkaline permanganate (Abstr., 1891, 576), when oxidised with alkaline permanganate on the water bath, yield a bibasic *acid* which forms hard granules or minute needles which soften at 170°. It forms a *potassium salt*, $C_9H_{13}O_4K + C_9H_{14}O_4 + 7H_2O$, crystallising in minute needles, and is possibly identical with the isocamphopyric acid prepared by Marsh, Balliol, and Gardner by distilling camphoic acid

(Trans., 1891, 651). By reducing digitogenic acid with sodium amalgam, *dioxydigitogenic acid*, $C_{14}H_{22}O_3 + \frac{1}{2}H_2O$, is obtained; it forms minute, nacreous plates, and begins to soften at about 240°. When digitogenic acid is boiled with potash and dilute alcohol, carbonic anhydride is eliminated, and two acids are formed; of these, *hydrodigitoic acid*, $C_{13}H_{22}O_3$, occurs in far smaller quantity; it softens at 240°, crystallises from 93 per cent. alcohol in silky needles, and yields a *magnesium salt*, $(C_{13}H_{21}O_3)_2Mg + 5H_2O$, forming white, nodular aggregates. By the cautious addition of water to the alcoholic mother liquor, and allowing the mixture to remain for a time, colourless prisms of *digitoic acid*, $C_{13}H_{20}O_3 + \frac{1}{2}H_2O$, are deposited; this acid melts at 210°, yields a *magnesium salt*, $(C_{13}H_{19}O_3)_2Mg + 8H_2O$, crystallising in nodular aggregates with a greasy lustre, and is converted by further oxidation into digitic acid. C. F. B.

Crystalline Substance from Santalum Praesii. By A. Berkenheim (*J. Russ. Chem. Soc.*, **24**, 688—690).—The author has investigated a crystalline substance obtained by Schimmel and Co. from *Santalum Praesii*. On recrystallisation, it forms large prisms melting at 101—103°, and having the composition represented by the formula $C_{15}H_{24}O_2$. On heating with acetic anhydride, it gives an acetate, $C_{15}H_{23}O_2Ac$, which crystallises in large, hexagonal plates, and melts at 68·5—69·5°. Phosphorus pentachloride has no action on the acetate, but phosphorus trichloride, with the original substance, gives a chloro-derivative, $C_{15}H_{23}OCl$, which melts at 119—120·5°. The original substance gives a sodium derivative from which the methyl ether is obtained in the liquid state. Oxidation with potassium permanganate yields an acid $C_7H_{14}O_2$. J. W.

Gum Benzoïn from Siam. By F. Lüdy (*Arch. Pharm.*, **231**, 461—480; compare this vol., i, 480).—Gum benzoïn (from Siam) is soluble in ether, and the dissolved substance yields no ash when ignited. It contains (1) vanillin, 0·15 per cent.; (2) free benzoic acid; (3) 0·3 per cent. of an oily, neutral substance which is an ethereal salt of benzoic acid; (4) a mixture of a little *benzoresinylic benzoate* with much *siaresinotannylic benzoate*, this mixture forming the main constituent of the gum. In addition to these, woody impurities are present to the extent of 1·6—3·3 per cent. No cinnamic acid, either free or combined, could be detected. By hydrolysis of the mixture of benzoresinylic and siaresinotannylic benzoates, benzoic acid and a mixture of benzoresinol and siaresinotannol are obtained in the proportion of about 1 : 11. The benzoresinol is identical with the substance obtained from Sumatra benzoïn; it crystallises from acetone in groups of long, white prisms, and melts at 272° (uncorr.). *Siaresinotannol*, $C_{12}H_{14}O_3$, is a brown powder, resembling in its properties the resinotannol obtained from Sumatra benzoïn. It yields a *potassium derivative*, $C_{12}H_{13}O_3K + H_2O$, crystallising in yellow needles, and an *acetyl derivative*, $C_{12}H_{13}AcO_3$, as a yellow, amorphous powder. Nitric acid has the same action on it as on Sumatra resinotannol. C. F. B.

A Ketone obtained from Ethylic Dihydrocollidinedicarboxylate. By F. Garelli (*Gazzetta*, **23**, i, 569—579).—Amongst the products obtained by Hantzsch (Abstr., 1886, 77) on heating ethylic dihydrocollidinedicarboxylate with dilute hydrochloric acid in a closed tube at 120°, is a ketone of the composition $C_8H_{12}O$.

When this ketone is heated with alkali and benzaldehyde, it yields a condensation product of the composition $C_{15}H_{16}O$; this crystallises in beautiful rosettes melting at 99°. It gives a crystalline *oxime* which melts at 133—134°, and is soluble in alcohol, ether, benzene, and acetic acid; no acetyl derivative could be prepared from it. The *hydrazone*, $C_{15}H_{16}{:}N_2HPh$, is obtained in small, yellow needles melting at 180°. The condensation product is readily oxidised by dilute alkaline permanganate, yielding benzoic and acetic acids.

W. J. P.

Cryoscopic Behaviour of some Acetates of Feeble Bases. By A. Ghira (*Gazzetta*, **23**, i, 341—346; compare Konovaloff, this vol., ii, 357, and Nasini and Pezzolato, *ibid.*, i, 444).—The author has determined the molecular depressions of the freezing points of water and benzene by the acetates of aniline, pyridine, diethylaniline, nicotine, quinoline, diisoamylamine, diisobutylamine, propylamine, and allylamine, and by acetanilide. In aqueous solution, all these substances behave as if completely dissociated; the benzene solutions, however, show considerable diversity of behaviour. Nicotine acetate in dilute benzene solutions gives almost normal molecular depressions, whilst aniline acetate, under similar circumstances, seems to behave as a mixture of the base with acetic acid.

W. J. P.

Derivatives of Quinoline. By A. Claus (*J. pr. Chem.* [2], **48**, 135—140).—In reviewing the present state of our knowledge as to the orientation of quinoline substitution products, the author points out that the nitro- and sulphonic radicles invariably enter the benzene ring, whereas bromine will always take the 4′ position if this be unoccupied; chlorine, on the other hand, does not show this affinity for the 4′-position. With regard to the influence of already existing substituting groups on the orientation of entering groups, it is noted that the existence of bromine in the benzene ring does not influence the entry of a new bromine atom into the 4′-position. The case is somewhat different when hydroxy-groups occur in the benzene ring. Thus it has been shown (Abstr., 1892, 353) that the first bromine atom which enters into 1- and 3-hydroxyquinoline gives rise to a 4-bromo-derivative; the same holds good for the entry of a chlorine atom into these hydroxyquinolines, nor will the second bromine or chlorine atom take the 4′-position. A third bromine atom can be introduced into 1-hydroxyquinoline by treatment of 1 : 4-hydroxyquinolinesulphonic acid with phosphorus bromide, and this atom takes the 4′-position; but in this respect chlorine and bromine differ, for no trichloro-1-hydroxyquinoline, containing a 4′-chlorine atom, has yet been prepared.

The entry of bromine into a quinoline-1-sulphonic acid may take place either in the 3- or 4′-position, according to the experimental conditions.

A. G. B.

1-Chloroquinoline. By A. Claus and M. Schöller (*J. pr. Chem.* [2], **48**, 140—151).—1-*Chloroquinoline*, prepared from orthochloraniline by Skraup's method, is a nearly colourless oil, which quickly becomes brown on exposure to light and air; it boils at 288°, and is not solid at −20°; it is freely soluble in most organic solvents, and markedly soluble in water. If crude chloraniline, containing both the ortho- and the para-compounds, be employed for making 1-chloroquinoline, the latter can afterwards be separated from the 3-chloroquinoline by dissolving the mixture in alcohol and adding nitric acid, when the 3-derivative is precipitated as nitrate. 1-*Chloroquinoline hydrochloride* crystallises in colourless needles, melts in its water of crystallisation at 96—97°, and dissolves freely in alcohol and in water. The *platinochloride*, $(C_9NH_6Cl)_2,H_2PtCl_6 + 2H_2O$, forms small, yellow needles, and melts, when anhydrous, at 235° with decomposition. The *nitrate* melts in its water of crystallisation at 86—87°, and dissolves freely in water, but less freely in alcohol. The *dichromate*, $(C_9NH_6Cl)_2,H_2Cr_2O_7$, crystallises in lustrous, orange laminæ, melts, with carbonisation, at 160—161°, and dissolves freely in hot water. The *methiodide*, C_9NH_6Cl,MeI, crystallises in hard, yellow needles and short prisms, darkens and melts at 165°, and dissolves in hot water and alcohol, but not in ether. The *methochloride* crystallises in colourless laminæ and flat prisms, melts at 140°, and dissolves in water; its *platinochloride*, $(C_9NH_6Cl,MeCl)_2,PtCl_4$, melts, with decomposition, at 248°.

4 : 1-*Nitrochloroquinoline* is the sole product of the nitration of 1-chloroquinoline; it crystallises in thin, colourless needles, melts at 144°, and dissolves in hot alcohol and in ether. The *platinochloride* is anhydrous, and melts with decomposition at 260°.

4 : 1-*Amidochloroquinoline*, obtained in the usual way, crystallises in lustrous, colourless aggregates of needles, which soon become yellow or red; it melts at 152°, and is not volatile with steam; organic solvents dissolve it freely. The *hydrochloride* crystallises in brilliant, thick, red, anhydrous prisms, and melts at 275°; the *platinochloride*, with $2H_2O$, is described. 1 : 4-*Chloroquinoline diazochloride* forms red needles; by treatment with cuprous chloride, it yields 1 : 4-dichloroquinoline, melting at 94°, identical with that prepared by La Coste (Abstr., 1882, 979); its *platinochloride* melts at 252° with decomposition.

1 : 4-*Chloroquinolinesulphonic acid* crystallises with $2H_2O$ in brilliant, colourless, transparent, lustrous prisms or needles, and in rhombic tables; it has no definite melting point. The *ammonium* salt is described, as are also the *sodium* salt, with $5H_2O$; the *barium* salt, with $7H_2O$; the *silver* salt; the *copper* salt, with $4H_2O$; and the *ethylic* salt, melting at 140°. A. G. B.

1-Bromoquinoline. By A. Claus and H. Howitz (*J. pr. Chem.* [2], **48**, 151—160).—1-Bromoquinoline (Abstr., 1888, 163) is a colourless, or pale yellow, oil; it boils at 302—304°, and is not solid at −10°. The platinochloride crystallises with $2H_2O$ and also with $3H_2O$, and melts with decomposition at 252°. The *methiodide*, C_9NH_6Br,MeI, forms long, yellow, anhydrous needles and prisms, and

melts at 280—281°. The *ethiodide* crystallises in yellowish-green needles or thick, yellow, prismatic aggregates, and melts at 183° with gradual decomposition.

4:1-*Nitrobromoquinoline* crystallises in colourless needles, melts at 137—138°, and sublimes unchanged; its *platinochloride* is described. 4:1-*Amidobromoquinoline* forms yellow needles or thick prisms, melts at 128—130°, and sublimes; it dissolves in acids with an intensely red coloration, and is precipitated from these solutions by ammonia; its *platinochloride* is described. 4:1-*Dibromoquinoline* was obtained from the amido-derivative through the diazo-reaction; it crystallises in long, colourless needles, and melts at 127°. A *compound* melting at 162°, whose nature has yet to be elucidated, was formed at the same time.

1:4'-*Amidobromoquinoline*, prepared from the nitro-4'-bromoquinoline (m. p. 124°) which is always formed as a bye-product in the preparation of 4:4'-nitrobromoquinoline, crystallises in long, straw-coloured needles, melts at 107—108°, and dissolves in alcohol. The *hydrochloride* melts with decomposition at 252°; the *platinochloride* is described. As the amido-derivative yields 1:4'-dibromoquinoline (Abstr., 1890, 1320) through the diazo-reaction, the orientation of the parent nitro-derivative is settled as 1:4'-nitrobromoquinoline.

A. G. B.

Iodoquinolines. By A. Claus and P. Grau (*J. pr. Chem.* [2], **48**, 160—169).—1-*Iodoquinoline* is prepared by diazotising 1-amidoquinoline and treating the diazo-compound with potassium iodide and copper; it crystallises in colourless, vitreous needles, which become brown when exposed to light and air; it melts at 136° and dissolves in hot water and in most organic solvents. The *hydrochloride*, C_9NH_6I,HCl, crystallises in short, thick, yellow prisms, and melts at 183°; the *platinochloride* is described. Halogen alkyl compounds and nitro-derivatives have not been obtained. The *dichromate*,

$$(C_9NH_6I)_2,H_2Cr_2O_7,$$

melts with decomposition at 135°; the *nitrate*, also with decomposition, at 154°.

3-*Iodoquinoline*, prepared from 3-amidoquinoline, crystallises in nacreous, nearly colourless laminæ, and sublimes in the form of needles; it melts at 88° and dissolves in hot water and in most organic solvents. The *dichromate*, the *hydrochloride*, melting at 210°, and the *platinochloride*, melting with decomposition at 265°, are described. The *methiodide* crystallises in brilliant, yellow, transparent, vitreous prisms and long needles, and is unchanged at 300°.

4-*Iodoquinoline*, from 4-amidoquinoline, crystallises in small, colourless, vitreous needles and sublimes in the same form; it melts at 100° and dissolves very slightly in hot water, but freely in most organic solvents. The *dichromate* melts with decomposition at 165°; the *hydrochloride* becomes dark and melts at 235°; the *platinochloride* melts with decomposition at 263°; the *methiodide* crystallises in fern-like aggregates of small, yellow needles, and melts with decomposition at 245°.

2-*Iodoquinoline*, from 2-amidoquinoline (see next abstract), forms

small, colourless needles, melts at 103°, and resembles the foregoing iodoquinolines in properties. A. G. B.

2-Nitroquinoline and its Derivatives. By A. Claus and C. Massau (*J. pr. Chem.* [2], **48**, 170—179).—2-Nitroquinoline has been already described (Abstr., 1888, 295); it crystallises in plates or needles, and melts at 132—134°. The *methiodide* forms brilliant, dark red, transparent crystals of various ill-defined forms, and melts at 231—233° with decomposition. The *methochloride* melts with decomposition at 212—213°. The *methonitrate*, obtained by acting on the methiodide with silver nitrate, crystallises in prisms and melts with decomposition at 170°. The *ethiodide* melts with decomposition at 220°.

2-*Amidoquinoline* crystallises in yellowish-white needles, which are unstable in air; it is very slightly volatile with steam, melts at 188—190°, and sublimes. The *platinochloride* melts with decomposition at 225°. The conversion of 2-amidoquinoline into 2-hydroxyquinoline may be effected through the diazo-reaction, but better by heating with hydrochloric acid at 220°; the preparation of the corresponding bromo-, chloro-, and iodo-derivatives from the amidoquinoline may also be effected through the diazo-reaction.

A. G. B.

Hydroxy-derivatives of Anthraquinolinequinone. By C. Graebe and A. Philips (*Annalen*, **276**, 21—35).—Bohn obtained certain blue and green dyes by heating dihydroxyanthraquinolinequinone ("alizarin-blue") with ordinary or fuming sulphuric acid (Badische Anilin- und Soda-Fabrik, German Patents of 1888, Nos. 46654 and 47252). These dyes have been shown by Graebe (Abstr., 1891, 463) to contain higher hydroxy-derivatives (compare also Schmidt and Gattermann, Abstr., 1891, 1382); subsequently, the method was extended by Bohn and by Schmidt and Gattermann (Abstr., 1891, 935) to the preparation of polyhydroxy-derivatives of anthraquinone from alizarin.

The authors find that the derivatives of anthraquinolinequinone, like the corresponding ones of anthraquinone, are the "darker" in colour the more hydroxyl groups they contain (compare below).

Hydroxyanthraquinolinequinone, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)<\begin{matrix}CH{:}CH\\N{=}CH\end{matrix}$ [OH = 3′ or 4′], is prepared as follows:—"Alizarin-blue" is converted into amidohydroxyanthraquinolinequinone by heating it at 160° with aqueous ammonia of 0·95 sp. gr.; the amido-derivative is then dissolved in concentrated sulphuric acid mixed with one-fourth its volume of water, treated at 0° with sodium nitrite, and the liquid poured into boiling alcohol and boiled for a quarter of an hour; the hydroxyanthraquinolinequinone is precipitated by the addition of water. It crystallises in brick-red prisms, melts at 208°, and is as good as insoluble in water, sparingly soluble in ether, but more readily in alcohol. It dissolves in concentrated sulphuric acid with a yellowish-brown coloration, the sulphate being precipitated on diluting with water; in ammonia, it dissolves with a cherry-red colora-

tion, and in alkalis with a violet coloration; in presence of an excess of alkali, and especially on boiling, the violet alkali salts separate. The *benzoyl* derivative, $C_{17}NH_8O_2{\cdot}OBz$, forms brown crystals, and melts at 175°.

Trihydroxyanthraquinolinequinone [$(OH)_3$ = 3′ : 4′ : 4 or 3′ : 4′ : 1] ("hydroxyalizarin-blue") may be obtained from the portion of crude "alizarin-green" (not the bisulphite compound) which is insoluble in nitrobenzene, by heating it at 180° with hydrochloric acid or by sublimation; it is, however, best prepared by Schmidt and Gattermann's method (Abstr., 1891, 1383). The absorption spectrum of the solution in alcoholic ammonia is almost the same as that of "alizarin-blue," and its solution in concentrated sulphuric acid exhibits an absorption band at 40—45, and a lighter one at 50—56 (Bunsen-Kirchhoff scale). It differs from "alizarin-blue" in being insoluble in aqueous ammonia.

Tetrahydroxyanthraquinolinequinone [$(OH)_4$ = 3′ : 4′ : 4 : 1] ("dihydroxyalizarin-blue") occurs in small quantity in technical "alizarin-green" and in "alizarin-indigo-blue." When "alizarin-green" is extracted with boiling nitrobenzene, the tetrahydroxy-derivative separates from the filtrate in dark blue crystals; it is also obtained as a sublimate when "alizarin-indigo-blue" is heated. It is insoluble in aqueous ammonia, and is identical with the compound prepared by Schmidt and Gattermann (*loc. cit.*). Its solution in concentrated sulphuric acid exhibits a bright, broad band in the red region at 34—40, and a narrower one in the yellow at 47—51.

Pentahydroxyanthraquinolinequinone [$(OH)_5$ = 3′ : 4′ : 4 : 2 : 1 or 3′ : 4′ : 4 : 3 : 1 ?] represents the portion of "alizarin-indigo-blue" soluble in nitrobenzene; it forms a blue, crystalline mass, and is soluble in both aqueous and alcoholic ammonia, as well as in alkalis, forming blue solutions. Its solution in alcoholic ammonia exhibits two faint absorption bands, a narrow one at 37—38 and a broad one at 42·5—48. The absorption spectrum of the solution in concentrated sulphuric acid resembles that of the tetrahydroxy-derivative, but the bands are less distinct, especially that in the yellow region. The *pentabenzoyl derivative* is a reddish-brown, flocculent substance; it melts at 175°, and yields the pentahydroxy-compound when boiled with aqueous alkalis.

As stated by Schmidt and Gattermann, "alizarin-blue-green" contains the sulphonic acid of a trihydroxyanthraquinolinequinone, and "alizarin-green" contains an isomeric acid; the authors have also detected varying amounts of tetrahydroxyanthraquinolinequinone in the last-mentioned dye. "Alizarin-indigo-blue" consists of a mixture of tetra- and penta-hydroxyquinolinequinones.

The authors show that the above-described colouring matters derived from "alizarin-blue" yield quinolinic acid on oxidation with nitric acid, which fact proves that the hydroxyl group and also the sulphonic group in these dyes always enters the benzene nucleus, and not the pyridine nucleus. A. R. L.

Pyrazole Compounds. By O. Severini (*Gazzetta*, **23**, i, 284—286).—The action of sodium hypochlorite on pyrroline has been

already investigated by Ciamician and Silber (*Gazzetta*, **16**, 19). On boiling 1-phenylpyrazole with sodium hypochlorite solution, *1-phenylchloropyrazole*, $C_9H_7N_2Cl$, is obtained; it is very volatile, and forms beautiful white needles melting at 75—75·5°. It is insoluble in water, but soluble in alcohol or ether. The chlorine probably occupies the position 4 of the pyrazole nucleus, for sodium hypochlorite does not act on 1-phenyl-4-bromopyrazole. W. J. P.

Phenylethyldimethylpyrazole. By L. Balbiano (*Gazzetta*, **23**, i, 323—332; compare Abstr., 1892, 885).—*1-Phenylethyldimethylpyrazole*, $C_3N_2PhEtMe_2$, is obtained by the action of phenylhydrazine on β-acetylpropionylethane in ethereal solution; it is a yellow oil with an aromatic odour, and boils at 150° under 75 mm. pressure. It is soluble in alcohol or ether, but insoluble in water, and gives the pyrazoline reaction on boiling with soda, and subsequently acidifying and treating with potassium chromate, ferric chloride, or sodium nitrite solution. The *platinochloride*, $(C_3N_2PhEtMe_2)_2,H_2PtCl_6 + 2H_2O$, forms beautiful reddish-yellow laminæ, and melts at 175° with decomposition. On heating at about 230°, it absorbs oxygen and yields trioxymethylene and a bright-yellow powder of the composition $(C_3N_2PhEtMe)_2PtCl_2$. The latter substance, on warming with nitrohydrochloric acid, yields *dichloroplatomethylethylphenyltrichloropyrazole*, $(C_{12}H_{10}N_2Cl_3)_2PtCl_2$, as a crystalline powder which is insoluble in water or alcohol.

The author concludes that the platinochlorides of tetra-substituted derivatives of pyrazole undergo the same change on heating as do those of tri-substituted derivatives. W. J. P.

Synthesis of Homologues of 1-Phenylpyrazole. By L. Balbiano and G. Marchetti (*Gazzetta*, **23**, i, 485—492).—*1-Phenylpyrazole methiodide*, $CH\begin{matrix}<\\ \end{matrix}\begin{matrix}CH{\cdot}NPh\\ |\\ CH{:}N,MeI\end{matrix}$, is obtained, in almost quantitative yield, by heating the pyrazole with methylic iodide in a closed tube at 100°; it forms beautiful, lustrous needles which melt at 178—179° with decomposition, is soluble in water or alcohol, and insoluble in ether. When heated in a closed tube at 240—300°, it yields a mixture of phenylpyrazole and *1-phenyl-4-methylpyrazole*, $C_3N_2H_2MePh$, a yellowish oil which has an aromatic odour, boils at 264—265°, and does not solidify at −15°; it is insoluble in water. The *platinochloride*, $(C_3N_2H_2MePh)_2,H_2PtCl_6,2H_2O$, separates from water in yellowish-red needles which melt at 159—160° with decomposition; it loses its water in a vacuum over sulphuric acid. When the anhydrous salt is heated at 130—160°, it gives *dichloroplato-1-phenyl-4-methylpyrazole*, $(C_3N_2H_2MePh)_2PtCl_2$, as a bright-yellow powder which is insoluble in water, and does not melt at 250°. *1-Phenyl-4-methylpyrazole methiodide*, $C_3N_2H_2MePh,MeI$, is obtained by heating the pyrazole with methylic iodide at 100° in a sealed tube. It is soluble in alcohol and water and separates from the latter solvent in needles which melt at 160°; the corresponding ethiodide could not be prepared. On oxidation with alkaline permanganate, the pyrazole yields 1-phenylpyrazole-4-carboxylic acid. W. J. P.

Reduction of Substituted 1-Phenylpyrazoles. By G. Marchetti (*Gazzetta*, **23**, i, 425—430).—On reducing an alcoholic solution of 1-phenylpyrazole with sodium by the process previously given by the author (this vol., i, 177) no benzene is obtained and no reduction products could be isolated.

1-Phenyl-3 : 4-dimethylpyrazole, however, behaves like its 1 : 3 : 5-isomeride on reduction (this vol., i, 178), and the product of the reaction by similar treatment yields benzene, 3 : 4-dimethylpyrazole, and 1-*phenyl*-3 : 4-*dimethyltetrahydropyrazole*; the latter was obtained in very small quantity, and its properties could not be determined. It is energetically oxidised by cold permanganate just as its isomeride is. During the reduction, *dimethylphenyltrimethylenediamine* is also formed; the reduction hence proceeds partly as in the case of 1-phenyl-4 : 5-dimethylpyrazole. The new base has a pungent odour, but was not obtained in sufficient quantity for purification; on treatment with carbon bisulphide, it yields *dimethylphenyltrimethylenediamine trimethyltrimethyleneanilthiocarbamate*,

$$NHPh\cdot C_3H_4Me_2\cdot NH\cdot CS\cdot SH\cdot NH_2\cdot C_3H_4Me_2\cdot NHPh,$$

which crystallises in lustrous, white needles, and melts at 210° with slight decomposition.

3 : 4-*Dimethylpyrazole picrate* forms small needles melting at 155—156°, whilst its 3 : 5-isomeride melts at 158—159°.

W. J. P.

Some Acids of the Pyrazole Series. By L. Balbiano and O. Severini (*Gazzetta*, **23**, i, 309—319; 354—360).—1-*Phenylpyrazole*-4 : 5-*dicarboxylic acid*, $C_3N_2HPh(COOH)_2$, is obtained, together with a little oxalic acid, on oxidising 1-phenylmethylethylpyrazole with alkaline permanganate. The new acid crystallises in small, white, pearly laminæ, melting at 231·5° with decomposition; it is soluble in alcohol or hot water, but only sparingly so in ether or cold water. Its *dimethylic* salt forms hard, glossy tables melting at 84·5—85·5°, and is soluble in alcohol or ether, but insoluble in water; it is readily converted into the sodium salt by sodium ethoxide. On treating its alkaline solution with bromine, it yields a *dibromo*-derivative,

$$C_{11}H_6Br_2O_4N_2,$$

which may be extracted from the solution by ether after acidification; it forms small, yellow needles which melt at 197—199° with decomposition, and seems to be accompanied by a monobromo-derivative. On heating for seven hours at 240—255°, the dibromo-derivative loses carbonic anhydride and yields a *dibromophenylpyrazole*, $C_9N_2H_6Br_2$, which crystallises in white needles melting at 74°, and is soluble in ether and hot alcohol.

1-*Phenyl*-3 : 4-*dimethylpyrazole* is formed by the action of phenylhydrazine on an acidified solution of sodium ethoxide, methylethylacetone, and ethylic formate in ether. It is a pale-yellow oil of sp. gr. = 1·0747 at 0°, boils at 277—278°, and has an aromatic odour; it is soluble in alcohol and ether, insoluble in water, and gives a violet colour with ferric chloride. On oxidation with alkaline permanganate, it gives a mixture of 1-*phenyl*-3-*methylpyrazole*-4-*carboxylic* and

1-phenyl-4-methylpyrazole-3-carboxylic acids, which are separated by crystallisation from dilute alcohol. The former acid is the less soluble, and forms beautiful white needles melting at 191·5—192·5°; it gives a *calcium* salt which crystallises in small laminæ containing $3H_2O$. On heating the acid at 230—250° for 20 hours, carbonic anhydride is evolved, and 1-phenyl-3-methylpyrazole remains; the constitution of the acid is thus determined. The isomeric acid forms small, white laminæ which melt at 133·5—134·5°; its *calcium* salt is obtained in crystalline scales containing $2H_2O$. On oxidation with alkaline permanganate, both acids give *1-phenylpyrazole-3 : 4-dicarboxylic acid*, which crystallises in white laminæ melting at 200·5° with decomposition; it is soluble in alcohol or boiling water, but only sparingly so in ether. The *methylic* salt is obtained in long, white needles melting at 74·5—75·5°; it is soluble in alcohol and ether, but insoluble in water. W. J. P.

Pyrazole-3 : 5-dicarboxylic Acid. By G. Marchetti (*Gazzetta*, **23**, i, 567—569).—Buchner and Papendieck (this vol., i, 431) consider that the pyrazole-3 : 5-dicarboxylic acid obtained by them is not identical with that prepared by Marchetti (this vol., i, 179); their acid melted at 287—290°, whilst that prepared by Marchetti melted at 280°, a temperature, which, by a printer's error, was stated as 180°. The difference of 7—10° is due to the temperature being corrected in the one case and not in the other. Further, the barium salt crystallises with either 1 or 4 molecules of water. The two acids are therefore identical. W. J. P.

Platopyrazole Compounds. By L. Balbiano (*Gazzetta*, **23**, i, 524—529; compare Abstr., 1892, 885).—*1-Ethyl-3 : 5-dimethylpyrazole* is obtained by heating the silver derivative of 3 : 5-dimethylpyrazole with ethylic iodide and ether free from alcohol or water in a sealed tube at 100°; it is a slightly yellowish liquid, soluble in water and alcohol. The *platinochloride*, $(C_3N_2HMe_2Et)_2,H_2PtCl_6$, forms small, yellow needles melting at 173°, and is soluble in water or alcohol. On heating it at a little above the melting point, it loses hydrogen chloride, and *dichloroplato-1-ethyl-3 : 5-dimethylpyrazole*,

$$(C_3N_2Me_2Et)_2PtCl_2,$$

is obtained; this is a bright yellow powder, insoluble in water, and almost insoluble in boiling alcohol. The same compound is obtained on boiling the pyrazole with sodium platinochloride in aqueous solution; the reaction is, however, not complete.

The author has previously observed (Abstr., 1892, 885) that pyrazoles containing a substituted group in the position 4 of the nucleus do not react with sodium platinochlorides to give dichloroplato-derivatives. He now shows that 1-phenyl-4-methylpyrazole is not altered by boiling with aqueous sodium platinochloride; 1-phenyl-3-methylpyrazole, however, under similar conditions, gives rise to *dichloroplato-1-phenyl-3-methylpyrazole*, $(C_3N_2HMePh)_2PtCl_2$, a light yellow, crystalline powder. W. J. P.

Pyrazines and Piperazines. A Reply. By C. Stoehr (*J. pr. Chem.* [2], **48**, 191—192).—The author replies to some criticisms by Dennstedt (*ibid.*, **48**, 95) on some remarks contained in the author's recent paper on pyrazines (this vol., i, 486). A. G. B.

Constitution of Nicotine: Acetylnicotine. By A. Étard (*Compt. rend.*, **117**, 170—173).—When nicotine is heated at 150° with acetic anhydride, it is converted into *diacetylnicotine*, a syrupy liquid, which boils, with partial decomposition, at about 330°, and is not affected by alkalis. Its *platinochloride*, $C_{10}N_2H_{14}Ac_2O,HCl,PtCl_4$, crystallises well, and is reconverted into nicotine by hydrogen sulphide. The resistance offered by diacetylnicotine to the action of alkalis seems to indicate that it is an ammonium hydroxide, whilst the removal of the acetyl groups by hydrogen sulphide points to their close connection with nitrogen and platinum. The author suggests the formula $\begin{matrix}CH{:}CH\cdot C\cdot CHEt\cdot CH_2\\ C{=\!=}N\cdot C-NH-CH_2\end{matrix}$ for nicotine, and the formula

$$\begin{matrix}C{=\!=}CH\cdot C-CHEt-CH_2\\ CH{:}NHCl\cdot C\cdot NAc_2(OH)\cdot CH_2\end{matrix},PtCl_4$$

for the platinochloride. Jn. W.

Codeïne. By W. Göhlich (*Arch. Pharm.*, **231**, 235—290).—*Codeïne hydrobromide*, $C_{18}H_{21}NO_3,HBr + 2H_2O$, crystallises from alcohol in slender, colourless needles. The hydriodide is deposited from alcohol or ether with $1H_2O$, from water with $2H_2O$, and, contrary to the statement of Anderson (*Annalen*, **77**, 50), becomes anhydrous at 100°. The chromate, $(C_{18}H_{21}NO_3)_2,H_2CrO_4 + 5H_2O$, darkens on exposure to light. The *acetate*, $C_{18}H_{21}NO_3,C_2H_4O_2 + 2H_2O$, crystallises from ethylic acetate, and is extremely soluble in water. The *salicylate*, $C_{18}H_{21}NO_3,C_7H_6O_3$, is amorphous, and readily soluble in alcohol The *aurochloride* is a yellow, amorphous powder. The platinochloride precipitated from concentrated solutions is, at first, amorphous, but crystallises with $6H_2O$; a second modification, with $4H_2O$, crystallises directly from dilute solution; both compounds become anhydrous on heating at 100—104°. The mercurichloride, $(C_{18}H_{21}NO_3,HCl)_2,HgCl_2 + H_2O$, is deposited in stellate groups of colourless needles. Codeïne does not appear to combine with ethylenic chloride, but, on treatment with ethylenic bromide, an additive compound, $(C_{18}H_{21}NO_3)_2,C_2H_4Br_2$, is formed, which could not be obtained in crystals; it yields a pale yellow, amorphous *platinochloride*.

A comparison of the properties and reactions of v. Gerichsten's crystalline "chlorocodide," $C_{18}H_{20}ClNO_3$ (*Annalen*, **210**, 107), with the amorphous substance prepared by Matthiessen and Wright (*Annalen*, Sup., **7**, 371) shows that they are identical; the latter compound, after purification, crystallises from light petroleum. Chlorocodide gives a yellow coloration with nitric acid, but with sulphuric acid it is almost colourless; Fröhde's reagent gives a yellowish-green colour, changing to blue on heating; Erdmann's reagent, a yellowish-brown,

which becomes red on warming; with vanadic anhydride and sulphuric acid, a yellow coloration is produced, which turns bluish-green on heating.

Chlorocodide aurochloride, $C_{18}H_{20}ClNO_2,HAuCl_4$, is golden yellow and amorphous, and melts at 171—172° with decomposition. Chlorocodide is not acted on by tin and hydrochloric acid, by sodium and alcohol, or by silver oxide, but, on heating with alcoholic potash at 120—130°, it is converted into apocodeïne. By the action of water on chlorocodide at 140—150°, codeïne is regenerated.

Sulphocodide, $C_{18}H_{20}NO_2,SO_3H + 5H_2O$, has previously been obtained by Anderson (*loc. cit.*), and is prepared by the action of concentrated sulphuric acid on codeïne for 24 hours at ordinary temperatures; it is a neutral compound, crystallising from water in colourless needles, which decompose, without melting, at about 246°. Sulphocodide gives a violet-red coloration on warming with sulphuric acid; the addition of a drop of nitric acid to this solution changes the colour to dark brown and finally to yellow. With concentrated sulphuric acid and cane sugar, a bluish-green coloration is obtained, changing to purple-red on heating. On warming with ferric chloride and concentrated sulphuric acid, it gives an indigo-blue coloration, becoming blood-red on the addition of nitric acid. With concentrated nitric acid alone, at ordinary temperatures, the sulpho-derivative yields a cherry-red coloration which gradually disappears; Erdmann's reagent gives a greenish-blue changing to dull blue; Fröhde's reagent, on warming, a pale reddish-violet; sulphuric acid and vanadic anhydride produce a blue colour.

By the action of dilute sulphuric acid (1 : 1) on codeïne at 100°, a compound, termed by Anderson (*loc. cit.*) "amorphous" codeïne, is formed, which, on examination, proves to be identical with Merck's pseudocodeïne (Abstr., 1891, 1121); the *sulphate* crystallises with $2H_2O$ in tetragonal plates; the *aurochloride*, $C_{18}H_{21}NO_3,HAuCl_4 + 3H_2O$, is amorphous and golden-yellow. Armstrong (*Annalen*, **159**, 390) has prepared several of the salts of pseudocodeïne described by Merck (*loc. cit.*). Pseudocodeïne containes a methoxy-group, but no hydroxy-group, as is shown by its failure to form an acetyl derivative; with the ordinary alkaloïdal reagents, it behaves exactly like codeïne. J. B. T.

Quinine, Cinchonidine, and Conchinine. By O. Hesse (*Annalen*, **276**, 125—127).—When quinine hydrochloride is heated at 85° with hydrochloric acid of sp. gr. 1·189, the *dihydrochloride*, $C_{20}H_{25}ClN_2O_2,2HCl$, derived from Comstock and König's hydrochloroquinine is formed; when the salt is dissolved in concentrated sulphuric acid, a sulphonic acid is produced. A *base* giving a soluble crystalline tartrate is isolated from the mother liquor obtained in the preparation of the last-mentioned dihydrochloride; it is identical either with the author's isoquinine or with Skraup's pseudoquinine.

Hydrochlorocinchonidine resembles hydrochlorapocinchonidine very closely, but whether the two are identical has yet to be decided. A base, *pseudocinchonidine*, is obtained from the mother liquor from the hydrochlorocinchonidine.

Hydrochloroconchinine dihydrochloride yields a sulphonic acid crystallising with $10H_2O$ when dissolved in concentrated sulphuric acid; the *platinochloride* of this acid crystallises with $3H_2O$, and the *aurochloride* with $1H_2O$. The mother liquor from the hydrochloroconchinine dihydrochloride contains *α-isoconchinine*, a crystalline base, the *platinochloride* of which crystallises with $2H_2O$, and *β-isoconchinine*, an amorphous base. A. R. L.

Cinchonine. By O. Hesse (*Annalen*, **276**, 88—124).—The author has studied the action of sulphuric and hydrochloric acids on cinchonine, and has obtained 10 of the 16 theoretically possible isomerides.

Cinchonine was prepared from the commercial sulphate by first converting it into the hydrochloride, dissolving the latter in absolute alcohol, and treating the solution with hydrogen chloride, when the *dihydrochloride* separates in lustrous crystals, whilst hydrocinchonine remains dissolved. The *dihydrochloride*, $C_{19}H_{22}N_2O,2HCl$, is readily soluble in water, and has a specific rotatory power in aqueous solution ($p = 3$) $[\alpha]_{D15°} = +206{\cdot}1°$.

α-Isocinchonine is obtained when cinchonine dihydrochloride is heated at 85° for 48 hours with hydrochloric acid of sp. gr. 1·189; on concentrating the liquid, hydrochlorocinchonine dihydrochloride separates, and when the filtrate is shaken with ammonia and ether, pseudocinchonine is precipitated, and the α-isocinchonine is dissolved by the ether. The base melts at 126°, has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15°} = +51{\cdot}6$, and is identical with Comstock and König's isocinchonine and with Jungfleisch and Léger's cinchoniline.

Hydrochlor-α-isocinchonine, $C_{19}H_{23}ClN_2O$, is obtained, together with hydrochlorapoisocinchonine by the action of fuming hydrochloric acid at 140—150° on α-isocinchonine hydrochloride; it melts at 172°, and has a specific rotatory power in alcoholic solution $[\alpha]_{D15°} = 67{\cdot}6°$.

β-Isocinchonine is obtained by heating α-isocinchonine at 60—80° with concentrated sulphuric acid; it is identical with Jungfleisch and Léger's cinconigine, and is converted into apoisocinchonine when heated at 140—150° with hydrochloric acid of sp. gr. 1·125; if, however, it is heated with hydrochloric acid of sp. gr. 1·189 at the same temperature, hydrochlorapoisocinchonine is formed.

Apoisocinchonine is obtained by heating the hydrochloride of α- or β-isocinchonine with hydrochloric acid of sp. gr. 1·125 at 140—150°; it crystallises from aqueous alcohol in white needles, melts at 216°, and has a specific rotatory power ($p = 3$) $[\alpha]_{D15°} = +166{\cdot}8$.

Hydrochlorapoisocinchonine is formed when the hydrochloride of α- or β-isocinchonine is heated at 140—150° with hydrochloric acid saturated at 0°. When α-isocinchonine is used, the dihydrochloride of hydrochlor-α-isocinchonine occurs in the mother liquor. Hydrochlorapoisocinchonine forms white needles, melts at 203°, and has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15°} = +189{\cdot}8$. The *dihydrochloride* has a specific rotatory power in aqueous solution ($p = 3$) $[\alpha]_{D15°} = +172{\cdot}5$.

Homocinchonine (*Annalen*, **243**, 149) is obtained when cinchonine sulphate is heated at 140° with 25 per cent. sulphuric acid; it forms small, white prisms, melts at 251°, has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15°} = +208{\cdot}9$, and when dissolved in sulphuric acid at the ordinary temperature, yields a mixture of α- and β-isocinchonine, the former predominating.

Pseudocinchonine (see above) forms small, white needles, melts at 252°, and has a specific rotatory power in alcoholic chloroform solution ($p = 3$) $[\alpha]_{D15°} = +198{\cdot}4$.

Hydrochlorocinchonine (Comstock and Königs) is obtained by treating cinchonine hydrochloride with fuming hydrochloric acid at 85°.

Hydrochlorapocinchonine (*Annalen*, **205**, 348) is formed by heating cinchonine or apocinchonine with fuming hydrochloric acid at 140°. The *sulphonic acid*, $C_{19}H_{22}ClN_2O{\cdot}SO_3H$, is obtained by dissolving the base in concentrated sulphuric acid at the ordinary temperature; it is anhydrous, sparingly soluble in water, and melts at 227°.

Apocinchonine (*Annalen*, **205**, 330) melts at 228° (not 209°), and has a specific rotatory power in alcoholic chloroform ($p = 3$) $[\alpha]_{D15°} = +197{\cdot}5$.

Isoapocinchonine is obtained by heating the dihydrochloride of hydrochlorocinchonine or hydrochlorapocinchonine with water in a sealed tube at 140°; it forms white prisms, melts at 232—234°, and has a specific rotatory power in alcoholic solution ($p = 3$) $[\alpha]_{D15°} = +186{\cdot}2°$.

Diapocinchonine is obtained by heating α-isocinchonine at 140—150° with hydrochloric acid of sp. gr. 1·125. A determination of the molecular weight by the cryoscopic method showed that it is an isomeride of cinchonine.

Dicinchonine (*Annalen*, **227**, 153) is isomeric and not polymeric with cinchonine. A. R. L.

Benzoylcinchonine. By E. Léger (*Compt. rend.*, **117**, 110—112). —Benzoylcinchonine, prepared by Schützenberger's method, crystallises from absolute ether in colourless and odourless prisms, insoluble in water, but very soluble in aqueous alcohol or aqueous ether, although much less soluble in anhydrous ether. The crystals are anhydrous, soften at 103°, and melt at 105—106° (uncorr.). Benzoylcinchonine, unlike cinchonione, is lævogyrate, and at 24° $[\alpha]_D = -22{\cdot}26°$ to $-25{\cdot}35°$, the rotatory power, in alcoholic solutions, increasing with the concentration. In acidified alcoholic solutions, the rotatory power diminishes as the proportion of acid increases, and may even change its sign—

1 mol. HCl.... $[\alpha]_D = -19{\cdot}67°$	2 mols. HCl.... $[\alpha]_D = -16{\cdot}72°$
½ mol. H_2SO_4.. $[\alpha]_D = -17{\cdot}18°$	1 mol. H_2SO_4... $[\alpha]_D = +10{\cdot}68°$

Various salts have been prepared. The basic hydrochloride crystallises in transparent tablets, the normal hydrochloride in needles containing $1C_2H_6O$, the basic hydrobromide in needles containing $1H_2O$, and the platinochloride in golden-yellow needles. The alkyl derivatives as a rule crystallise well. C. H. B.

Cinchonibine. By E. Jungfleisch and E. Léger (*Compt. rend.*, 117, 42—44).—The variations observed in the proportions of cinchonifine, apocinchonine, and cinchonibine obtained from cinchonine are due to the fact that cinchonibine splits up into cinchonifine and apocinchonine. When converted into a methochloride, cinchonibine yields apocinchonine methochloride in large, monoclinic prisms containing $4H_2O$ and cinchonifine methochloride in prismatic needles containing $2H_2O$.

When cinchonibine is converted into basic succinate, it yields large, hexagonal crystals, which contain $6H_2O$, and are very different in appearance from cinchonifine succinate, but crystallographically identical with the succinate prepared from pure apocinchonine. Further, if increasing quantities of cinchonifine are added to the apocinchonine, the succinate always has the same form, and it follows that basic apocinchonine succinate has the power of taking up large quantities of cinchonifine succinate without any change in appearance. If a mixture of equal weights of cinchonifine and apocinchonine is converted into basic succinate, and the latter is decomposed by an alkali, it yields cinchonibine.

Cinchonibine can no longer be regarded as a true isomeride of cinchonine. It seems, however, to be a definite compound of cinchonifine and apocinchonine in equal proportions, and has the same properties, and, notably, the same rotatory power, when prepared by several different methods. Under the microscope, the crystals seem to be homogeneous. The compound remains unchanged when dissolved in a small quantity of alcohol, but splits up if a large quantity of the solvent is used. The rotatory power of cinchonibine solutions is the mean of the rotatory powers of cinchonifine and apocinchonine.

C. H. B.

Hyoscine and Oscine. By O. Hesse (*Annalen*, **276**, 84—86).—The aurochloride obtained from commercial hyoscine hydriodide has the composition $C_{17}H_{21}NO_4,HAuCl_4$, and melts at 198°. As thus prepared, it appears to contain a trace of an unknown alkaloïd, which does not, however, alter its composition.

The formula of benzoyloscine was erroneously given (Abstr., 1892, 1498) as $C_{15}H_{17}NO_4$; it should be $C_{15}H_{17}NO_3$. The formula of oscine aurochloride (*loc. cit.*) requires similar alteration. When benzoyloscine is warmed with hydrochloric acid, it decomposes into oscine and benzoic acid.

A. R. L.

Organic Bases in the Tubers of Stachys tuberifera. By A. v. Planta and E. Schulze (*Arch. Pharm.*, **231**, 305—313; compare this vol., ii, 53).—It has been previously shown that the tubers of *Stachys tuberifera* contain glutamine and tyrosine (Abstr., 1890, 1183); two other nitrogenous bases have now been isolated, one of which occurs in very small quantity, and has not hitherto been investigated. The second compound, $C_7H_{13}NO_2$, which it is proposed to term *stachydrine*, is separated by means of auric chloride and purified by the help of the platinochloride; it is deposited from dilute alcohol in colourless, transparent crystals containing water of crystallisation. The base in aqueous solution is neutral to litmus, and, like the first

compound, is indistinguishable from betaïne by the ordinary alkaloïdal reagents. The *hydrochloride*, $C_7H_{13}NO_2,HCl$, crystallises from water or absolute alcohol in large, colourless prisms. The *platinochloride* crystallises with $2H_2O$ in flat, orange-red, rhombic prisms, $a : b : c = 0{\cdot}6082 : 1 : 0{\cdot}8277$. The *aurochloride* is deposited from water in small, yellow prisms. The *mercurochloride* and *nitrate* are colourless and crystalline. The *picrate* forms small, yellow prisms.

J. B. T.

Cryoscopy of Albumose and Peptone. By A. Sabanéeff (*J. Russ. Chem. Soc.*, **25**, 11—23).—A cryoscopic investigation of deutero-albumose from albumin, in aqueous solution, led to a molecular weight of about 3200; this number varied very little with the concentration of the solution. The molecule would thus seem to contain 2 atoms of sulphur. Proto-albumose has a somewhat similar molecular weight. The molecular weight of albumin-peptone (amphopeptone) is less than 400, increasing considerably with the concentration. The molecule of peptone contains no sulphur. J. W.

Nucleïnic acid. By A. Kossel and by J. Horbaczewski (*Chem. Centr.*, 1893, i, 787—788; from *Arch. Physiol.*, 1893, 107—115 and 157—164).—Nucleïc acid from yeast, on treatment with dilute acids, is resolved into a number of basic substances, and a compound which appears to be a pentose; it forms a *phenylglucosazone*, melting at 204—205°, and a *phenylhydrazone*, melting at 150°. *Plasmic acid*, $C_{15}H_{23}N_6P_6O_{20}$, is formed by the action of alkalis on nucleïc acid; on treatment with dilute acids, it yields a nitrogenous substance which has not been investigated, nucleïnic bases, guanine or adenine, and a compound of phosphorus which, in spite of Liebermann's statement to the contrary, is not metaphosphoric acid. The assertion that the nucleïc acids are compounds of metaphosphoric acid and albumin also lacks foundation, as is shown by a comparison of the natural and artificial products. The part played by nucleïc acid in the economy of the cell is discussed; it is probably actively engaged in the destruction of pathogenic micro-organisms and their products.

Horbaczewski's experiments on the formation of uric acid from spleen extract (Abstr., 1891, 1340) have been questioned, but he shows that the uric acid produced was pure and free from xanthine; the two compounds can be readily separated by precipitating the acid with ammonium chloride or hydrochloric acid. J. B. T.

Organic Chemistry.

Determination of Stereoisomerides. By E. Nickel (*Zeit. physikal. Chem.*, **12**, 275—279).—The author gives a convenient graphical method for determining the number and optical nature of stereoisomerides with a given number of asymmetric carbon atoms.

J. W.

Köhnlein's Method of preparing the Paraffins: Properties of Propane. By L. Meyer (*Ber.*, **26**, 2070—2073).—When secondary hexylic iodide, prepared from mannitol, is treated with aluminium chloride in a sealed tube, according to Köhnlein's method (*Ber.*, **16**, 560), ethane and butane are produced. The hexane chain has therefore been broken at the carbon atom with which the iodine is combined. Experiments are proceeding in order to ascertain whether this is a general reaction of the secondary iodides.

Propane can easily be liquefied at the atmospheric pressure by means of solid carbonic anhydride, and boils at −38° to −39°. The critical temperature is about 102°, the critical pressure being about 59 atmospheres. The following tables show the vapour pressure of the liquid and its specific gravity at various temperatures.

Temp.	Vapour pressure. Metres.	Temp.	Vapour pressure. Metres.
−33°	1·43	+5·5°	4·53
−19	2·08	12·5	5·41
−15	2·41	22·0	7·6
−11	2·78	34·0	10·5
− 5	3·16	53·0	18·9
− 2	3·71	85·0	35·0
+ 1	3·89	103·0	45·6

Temp.....	0°	6·2°	11·5°	15·9°
Sp. gr.....	0·535	0·526	0·519	0·512

A. H.

Oxidation of Chloroform with Chromic acid, and Preparation of Carbon Oxychloride from Carbon Tetrachloride. By H. Erdmann (*Ber.*, **26**, 1990—1994).—This paper opens with a short but valuable *résumé* of the subject. The oxidation of chloroform with sulphuric acid and potassium dichromate was studied by Emmerling and Lengyel in 1869; these chemists found but a small amount of carbon oxychloride among the products, and they incorrectly interpreted the reaction, inasmuch as they believed that chlorine is formed. The author states that the reaction is the following.

$$2CHCl_3 + CrO_3 + 2O = 2COCl_2 + CrO_2Cl_2 + H_2O.$$

Schützenberger showed, in 1869, that carbon oxychloride is obtained in good yield by the action of sulphuric anhydride on carbon tetra-

chloride. The following method of preparing carbon oxychloride is described by the author. Carbon tetrachloride (100 grams) is heated to boiling on a water bath in a flask furnished with a vertical reflux condenser; 80 per cent. anhydrosulphuric acid (120 c.c.) is run in drop by drop down the condenser, so that each drop comes into intimate contact with the ascending vapour of the carbon tetrachloride. The evolved carbon oxychloride passes, by a tube fused at right angles to the upper portion of the condenser tube, through concentrated sulphuric acid contained in a wash bottle (which is kept in water during the experiment), and thence to a Hofmann's receiver surrounded by a freezing mixture. When all the anhydrosulphuric acid has been run in, the globular flask is boiled over a free flame for five minutes. The yield of crude carbon oxychloride is 90 per cent. of the theoretical. It is rectified, the boiling flask being heated by the hand. The accompanying product is a mixture of pyrosulphuryl chloride, $S_2O_5Cl_2$, and chlorosulphonic acid, SO_3HCl; this mixture boils at 130—150°, and forms a valuable sulphonating agent. A. R. L.

Acrylonitrile. By Moureu (*Bull. Soc. Chim.*, [3], **9**, 424—427).—Acrylamide is distilled with twice its weight of phosphoric anhydride at 150—250°; about 30 per cent. of the theoretical yield of acrylonitrile is obtained. Its vapour density is 1·84. It is a colourless, mobile liquid soluble in water, having a feeble odour of hydrogen cyanide, and has no irritant action on the eyes; the sp. gr. = 0·843 at 0°. It boils at 78°, a temperature below that of the boiling points of acetonitrile (84°) and propionitrile (97°). It combines with bromine to form $\alpha\beta$-dibromopropionitrile, a liquid of sp. gr. 2·161 at 0°, insoluble in water, and intensely irritant in its action on the eyes.

β-Hydroxypropionitrile, although more stable than the corresponding acid, yields acrylonitrile when distilled with phosphoric anhydride. W. T.

Action of Iodine on Sodium Propoxide. By A. Kessler (*J. pr. Chem.*, [2], **48**, 236—240).—The action of iodine on sodium propoxide is similar to its action on sodium isobutoxide.

The propyl derivative of hydroxypropaldehyde,

$$OPr^{n}\cdot C_2H_4\cdot CH(OH)\cdot OPr^{n},$$

is obtained by gradually adding iodine to sodium propoxide, and cooling the mixture in ice-cold water; the product is then neutralised with tartaric acid, and fractionally distilled, when the ethereal derivative is precipitated as an oil, and is purified by distillation under diminished pressure. It distils at 111—114° under 26—28 mm. pressure, and is a colourless, highly refractive liquid having a characteristic odour. When heated in a sealed tube with acetic acid, it is converted into propylic acetate and a compound which the author believes to be hydroxypropaldehyde. This shows no fixed boiling point, the thermometer rising steadily from 100° to 170°; it has a characteristic odour, and quickly reduces ammoniacal silver solution.

A volatile acid was also obtained by the action of iodine on sodium propoxide, but it was not examined. E. C. R.

Myricyl Alcohol. By A. Gascard (*J. Pharm.*, [5], **28**, 49—54).—Myricyl alcohol has been prepared by the author from gum-lac, carnauba wax, and beeswax, and the product found to be identical in each case. Myricyl alcohol melts at 88°, and is a white solid, very slightly soluble in cold benzene, ether, or light petroleum, easily soluble in hot benzene, alcohol, and chloroform. On cooling the solutions, microscopic crystals are deposited, of which the form varies with the solvent; alcohol gives large, soft needles, benzene harder, feathery aggregates of nacreous lustre, and chloroform more aggregated forms.

Myricylic acetate is soluble in alcohol, benzene, and chloroform. It melts at 73°. Myricylic laurate (m. p. 69—70°) is less soluble in the same solvents. Myricylic palmitate (m. p. 75°), stearate (m. p. 78°), and arachidate (m. p. 84°) are insoluble in hot alcohol, but soluble in benzene. Myricylic cerotate (m. p. 87°) and melissate (m. p. 92°) are insoluble in boiling alcohol, and myricylic oleate (m. p. 65°) is but slightly soluble in alcohol. Myricylic benzoate crystallises from ether in fine plates melting at 70°. It is soluble in hot alcohol and cold benzene. Normal myricylic oxalate (m. p. 91°) is insoluble in boiling alcohol, and crystallises from benzene. Hydrogen myricylic phthalate is soluble in hot alcohol; the normal salt is insoluble in alcohol, but soluble in benzene. Both melt at 79°. W. T.

Raffinose and its Decomposition Products. By A. Aulard (*Bied. Centr.*, 1893, 703—704).—The best method for estimating raffinose in beet sugar is that introduced by Clerget with Herzfeld's modifications.

In the first products, neither Aulard nor Herzfeld could detect raffinose, and in the after products it was only present in small quantities.

The action of raffinose as affecting the formation of molasses cannot be expressed by a coefficient for the simple reason that it does not appear to exert any but a favourable influence on the crystallisation of saccharose, and it only appears in the final product, which consists of raffinose, saccharose, a few salts, and much organic matter.

Further, Aulard considers that, of all salts, organic calcium salts influence the formation of molasses least, and that crystallisation is not dependent on the presence of salts generally, but on the viscosity of the solution, which is itself limited by the presence of soluble organic calcium salts. E. W. P.

Combination of Iodine with Starch. By G. Rouvier (*Compt. rend.*, **117**, 281—282).—If an aqueous solution of starch is gradually mixed with iodine, it is found that iodine remains in the free state as soon as its proportion exceeds that required by the formula $(C_6H_{10}O_5)_{16}I_3$. It would seem, therefore, that there are three definite compounds of starch with iodine, $(C_6H_{10}O_5)_{16}I_2$, $(C_6H_{10}O_5)_{16}I_3$, $(C_6H_{10}O_5)_{16}I_4$. (Compare Abstr., 1892, 575, 801, and 1171.)

C. H. B.

Dextrin. By V. Griessmayer (*J. pr. Chem.*, [2], **48**, 225—230).—After reviewing the results obtained by other workers, the author concludes that in the reactions of the mash-tub a part of the molecule of the soluble starch is converted into amylodextrin, and of the six amylin groups of the latter, four are then converted into maltose (or isomaltose); the remainder is maltodextrin.

E. C. R.

Occurrence of Betaïne and Choline in the Sprouts of Barley and Wheat. By E. Schulze and S. Frankfurt (*Ber.*, **26**, 2151—2155).—The authors have succeeded in isolating and identifying betaïne and choline from the sprouts, or young seedlings, of barley (malt combs) and wheat. The method adopted was to extract the sprouts with water, treat the extract with lead acetate, and, after filtering, to precipitate the bases with phosphotungstic acid. The precipitate was then treated with milk of lime, the solution filtered, treated with carbonic anhydride, again filtered, neutralised with hydrochloric acid, and concentrated to a syrup. The hydrochlorides were extracted with hot alcohol, precipitated with an alcoholic solution of mercuric chloride, and the mercurichlorides separated by repeated crystallisation from water; or after crystallising them once or twice, the mercury was removed with hydrogen sulphide, and the hydrochlorides separated by means of cold absolute alcohol, in which choline hydrochloride dissolves, whilst betaïne hydrochloride does not.

C. F. B.

Oxidation of the Two Trithioacetaldehydes. By E. Baumann (*Ber.*, **24**, 2074—2079; compare Abstr., 1890, 25).—The oxidation of the stereoisomeric trithioacetaldehydes by means of potassium permanganate in the presence of sulphuric acid leads to the production of a disulphone sulphide, $C_6H_{12}S_3O_4$, and a trisulphone, $C_6H_{12}S_3O_6$, the products obtained from α- and β-trithioacetaldehyde being identical in every respect. The isomerism of these substances is therefore of a nature different from that of fumaric and maleïc acids, since the latter are converted by oxidation into optically isomeric products. Guareschi (Abstr., 1884, 294), who has also examined the action of potassium permanganate on trithioacetaldehyde, used impure material, and did not succeed in completely separating the products formed. The *disulphone sulphide* crystallises in long, transparent prisms or needles, which are odourless, and melt at 283—284°. It is the symmetrical trimethyl substitution product of the trimethylenedisulphone sulphide described by Camps (Abstr., 1892, 592), and has the formula $SO_2<\begin{matrix}CHMe-S\\CHMe\cdot SO_2\end{matrix}>CHMe$. It is moderately soluble in hot alcohol and acetic acid, but almost insoluble in chloroform, benzene, or ether. In contains one atom of hydrogen replaceable by metals, and is readily soluble in alkalis, but does not yield crystalline salts. It dissolves in concentrated acids on warming, and is reprecipitated by the addition of water. Fuming nitric acid partially oxidises it with production of a small amount of sulphuric acid, whilst a hot solution of potassium permanganate in the presence of dilute sulphuric acid slowly converts it into the trisulphone. The

properties of the latter substance will form the subject of a later publication. A. H.

Citronellaldehyde. By F. W. Semmler (*Ber.*, **26**, 2254—2258; compare Abstr., 1891, 539).—*Citronellaldoxime*, $C_{10}H_{18}NOH$, boils at 135—136° under 14 mm. pressure; the sp. gr. is 0·9055 at 20°/20°, and the molecular refraction 52·67.

The *nitrile of citronellaldehyde*, $C_{10}H_{17}N$, obtained by boiling the oxime with acetic anhydride, boils at 94° under 14 mm. pressure; the sp. gr. is 0·8645 at 20°/20°, and the molecular refraction 47·43.

Citronellic acid, $C_{10}H_{18}O_2$, is most easily obtained by treating the nitrile with alcoholic potash. It boils at 143·5° under 10 mm. pressure, and at 257° under atmospheric pressure; the sp. gr. is 0·9308 at 20°/20°, and the molecular refraction 49·60.

Dihydroxycitronellic acid $C_{10}H_{18}O_2(OH)_2$, is obtained by treating the preceding acid in very dilute solution with potassium permanganate at 0°. The *silver* salt is a white powder. The author was unable to obtain a lactone from this acid.

Citronellapimelic acid, $C_7H_{12}O_4$, is obtained by oxidising the preceding acid with chromic acid mixture. It crystallises in needles, and melts at 82—83°. The *silver* salt is a white powder insoluble in water.

The author concludes that citronellaldehyde (citronellal) has the constitution $CHO{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CH{:}CMe_2$. E. C. R.

Ketonic Compound from Tartaric acid. By E. Mulder (*Rec. Trav. Chim.*, **12**, 51—100; compare Abstr., 1890, 595; 1891, 830; 1892, 965).—In combining with ethylic chloride, ethylic disodiotartrate resembles ethylic sodacetoacetate (compare Nef, Abstr., 1892, 141). The copper derivative, $C_{16}H_{24}CuO_{11}$ (Abstr., 1892, 965) seems to be anhydrous; it begins to decompose at 115°, and to melt at 130°. When dissolved in absolute alcohol, and treated with a slight excess of alcoholic hydrogen sulphide, a crystalline *ketone*, $C_{16}H_{24}O_{10}$, is obtained; the aqueous solution of this substance gives a cherry-red coloration with ferric chloride, a precipitate with barium hydroxide, and a crystalline compound with phenylhydrazine. When the copper derivative is dissolved in dilute hydrochloric acid, and treated with phenylhydrazine, an oily compound is obtained.

The author was unable to prepare a crystalline copper compound from the insoluble portion of the product of the action of ethylic chloride on ethylic disodiotartrate.

Ethylic disodioracemate reacts with ethylic chloride, forming a soluble and an insoluble compound; the *copper* derivative obtained from the former has the same composition as that from ethylic disodiotartrate (dextro-); it, follows, therefore, that both the dextro- and lævo-tartaric acid derivatives react in an analogous manner.

A provisional study of the barium derivatives of the soluble and insoluble products of the action of ethylic chloride on ethylic disodiotartrate has revealed nothing definite up to the present; the author finds that the barium derivative of the insoluble portion of the product gives with hydrochloric acid and phenylhydrazine a

crystalline compound which resembles E. Fischer's pyruvic hydrazone, but is not identical with it.

Copper ethoxide is prepared by treating a solution of sodium ethoxide in absolute alcohol (pure) with anhydrous cupric chloride; it is a gelatinous compound of an indigo-blue colour.

An alcoholic solution of ethylic disodiotartrate yields a blue solution with cupric chloride, and gives no precipitate with anhydrous ferric chloride.

Copper pyruvate has the composition $(C_3H_3O_3)_2Cu + H_2O$, assigned to it by Berzelius (*Annalen*, **36**, 24); it is, however, crystalline.

The author was unsuccessful in preparing hydruvic acid by the method described by Böttinger (*Annalen*, **208**, 131), namely, treatment of basic barium pyruvate with carbonic anhydride.

By the action of sodium ethoxide on ethylic succinate in an atmosphere of hydrogen under reduced pressure, ethylic sodium succinate appears to be formed, but the tendency for the production of the closed chain compound, sodium succinosuccinate, is so great, that the alcohol, which probably combines with the succinate initially formed, cannot be eliminated. A. R. L.

Ethylic Orthoformates. By J. Walter (*J. pr. Chem.*, [2], **48**, 231—235).—Ethylic orthoformate may be obtained by adding a mixture of chloroform and alcohol to an aqueous solution of sodium hydroxide. The best yield was about 19 per cent. of the theoretical.

The author could not obtain a condensation product from ethylic orthoformate and diphenylamine. Trimethyltriphenylparaleucaniline is obtained by heating methyldiphenylamine, ethylic orthoformate, and zinc chloride on the water bath. E. C. R.

Diamidopropionic acid. By E. Klebs (*Ber.*, **26**, 2264—2267).—*Diamidopropionic acid hydrobromide*,

$$NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH,HBr,$$

is obtained by heating $\alpha\beta$-dibromopropionic acid with 20 molecular proportions of an aqueous solution of ammonia saturated at 0°. It crystallises in needles, darkens at 225°, melts at 228—230° with decomposition, shows a slight acid reaction with litmus, and is soluble in 12·5 parts of water at 20°.

Copper diamidopropionate, is obtained by treating the hydrobromide with lead hydroxide, then with hydrogen sulphide, and adding to the warm alkaline filtrate freshly-prepared copper hydroxide. It crystallises, with $4H_2O$, in violet-blue, monoclinic forms, and is dehydrated with difficulty. The dry salt absorbs water very energetically.

Diamidopropionic acid hydrochloride, obtained by treating the hydrobromide with lead hydroxide and then adding hydrochloric acid, is a white, crystalline powder, darkens at 220°, melts at 225° with decomposition, and is soluble in 11·57 parts of water at 20°. The

free acid is obtained by adding silver oxide to a solution of the hydrochloride, precipitating the dissolved silver with hydrogen sulphide, and evaporating the filtrate in a vacuum. It is a strongly alkaline syrup, solidifies when mixed with absolute alcohol and cooled, and is very hygroscopic. E. C. R.

Preparation of Normal Caproic and Hexylic acids. By J. TRIPIER (*Compt. rend.*, **117**, 282—284).—When castor oil and other vegetable oils are treated with nitric acid, the yield of heptylic acid is very small, and the result is not appreciably affected by variations in the concentration of the acid. Better results can, however, be obtained by using a mixture of nitric and sulphuric acids. 2000 c.c. of nitric acid is mixed with 500 c.c. of sulphuric acid, previously diluted with 2000 c.c. of water, and to this mixture is added 1000 c.c. of castor oil. The liquid is then heated until the reaction commences, and again after the effervescence has ceased, the product being distilled until about 2000 c.c. has passed over. After separation of the acid by means of a separating funnel, the 2000 c.c. of aqueous solution is treated with a further quantity of 500 c.c. of sulphuric acid and 2000 c.c. of nitric acid, in order to complete the oxidation.

Under these conditions, 1000 c.c. of castor oil yields about 500 c.c. of non-volatile bibasic acids, and 250 c.c. of volatile acids of the acetic series. The latter are mixed with a considerable proportion of normal heptylonitrile, but otherwise consist solely of normal hexylic and heptylic acids, in the proportion of 1 part of the former to 3 parts of the latter. C. H. B.

Di-γ-amidodipropylacetic acid and Octohydro-1 : 1′-naphtyridine. By A. REISSERT (*Ber.*, **26**, 2137—2144).—Using Gabriel's synthetic method (Abstr., 1890, 1129; 1891, 948), ethylic di-γ-phthalimidopropylmalonate, $C(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C_8H_4O_2N)_2(COOEt)_2$, has been prepared from sodium ethoxide, ethylic malonate, and γ-bromopropylphthalimide. When heated at 180° with hydrochloric acid, it is decomposed into phthalic acid, ethylic chloride, carbonic anhydride, and di-γ-amidodipropylacetic acid, $CH(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2{\cdot}COOH$; this acid, when distilled under atmospheric pressure, yields octohydronaphtyridine.

Ethylic di-γ-phthalimidopropylmalonate crystallises in soft, white needles, which melt at 155·5° (corr.). When boiled with strong aqueous potash, it is hydrolysed, and, if the product is neutralised and then shaken with benzoic chloride and soda, *di-γ-benzamidodipropylmalonic acid*, $C(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NHBz)_2(COOH)_2$, is obtained; this forms a white, sandy, crystalline mass, which softens when heated, and finally melts at 188—189°. The *silver*, $C_{23}H_{24}N_2O_6Ag_2$, and *barium*, $C_{23}H_{24}N_2O_6Ba$, *salts* are colourless, the latter crystalline. *Di-γ-amidodipropylacetic acid* is obtained, as above described, as the *hydrochloride*, with 2HCl, a white, hygroscopic substance. This is converted, by shaking with benzoic chloride and soda, into *di-γ-benzamidodipropylacetic acid*, which forms dull, white crystals, and yields a *silver salt*, $C_{21}H_{23}N_2O_4Ag$. Di-γ-amidodipropylacetic acid is itself obtained from

the hydrochloride by means of silver oxide; it forms a yellow oil, which distils unchanged under 35—40 mm. pressure. *Octohydronaphtyridine*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\\ |\qquad\qquad |\\ CH_2\cdot NH\cdot C{:}N\cdot CH_2\end{matrix}>CH_2$, obtained from it as described above, forms a yellowish oil, probably slightly impure; the *platinochloride*, $(C_8H_{11}N_2)_2,H_2PtCl_6$, crystallises in orange needles, and melts at 227° (uncorr.). C. F. B.

Action of Acrylic Chloride on Alcohols and Phenols. By Moureu (*Bull. Soc. Chim.*, [3], **9**, 415—417).—Ethereal salts of β-chloropropionic acid are formed by the action of acrylic chloride on alcohols and phenols. The products are identical with the ethereal salts prepared by the direct action of the alcohols on β-chloropropionic acid. Although hydrogen chloride is not evolved by the action of acrylic chloride on alcohols, the chloride itself does not absorb hydrogen chloride.

Methylic β-chloropropionate boils at 148°, and has a sp. gr. of 1·198 at 0°. Ethylic β-chloropropionate boils at 162°. Propylic β-chloropropionate has a very sweet and agreeable odour, a sp. of 1·092 at 0°, and boils at 179—181°. Isobutylic β-chloropropionate boils at 191—193°, and has a sp. gr. of 1·066 at 0°.

Phenylic β-chloropropionate is formed by the action of acrylic chloride (5 grams) on phenol (6 grams). The phenol is melted and mixed with the chloride, and, after 24 hours' contact, the product is distilled. A liquid of the composition $CH_2Cl\cdot CH_2\cdot COOPh$ passes over between 154° and 157° under a pressure of 30 mm. W. T.

Acrylic Anhydride. By Moureu (*Bull. Soc. Chim.*, [3], **9**, 413—415).—Finely powdered sodium acrylate (22 grams) is mixed with a little vaseline, and acrylic chloride (20 grams) added drop by drop, keeping the well-agitated mass cool. The reaction is completed by heating for half an hour on the water bath, and the product is then distilled under reduced pressure.

Acrylic anhydride, $(CH_2{:}CH\cdot CO)_2O$, decomposes partially on distillation, even in a vacuum. It is a colourless liquid of sharp odour; its action on the eyes is less violent than that of acrylic chloride; sp. gr. 1·094 at 0°. It is easily decomposed by water, and takes up the theoretical quantity of bromine at the ordinary temperature. It slowly decomposes, yielding a white, solid mass. W. T.

Constitution of the Unsaturated Acids obtained by boiling the Unsaturated βγ-Acids with Soda. By R. Fittig (*Ber.*, **26**, 2079—2081).—The author has compared the acid produced by boiling βγ-pentylenic acid (ethylidenepropionic acid) with soda with the αβ-pentylenic acid (propylideneacetic acid) prepared by Komnenos from propaldehyde and malonic acid; this reaction always yields a certain amount of the βγ-acid, in addition to the αβ-isomeride. In order to separate the two acids, their barium salts are repeatedly extracted with alcohol, and the more soluble portion used for the preparation of the

$\alpha\beta$-acid. The liberated acid is then warmed with sulphuric acid, which converts the $\beta\gamma$-derivative into valerolactone, whilst the pure $\alpha\beta$-acid is left.

This substance, which has not previously been obtained pure, solidifies, on cooling, in large plates or prisms, melting at 8—9°. It forms a characteristic *dibromide*, which crystallises well, is very readily soluble in light petroleum, benzene, &c., and melts at 55—56°. The acid also combines with hydrogen bromide to form *β-bromovaleric acid*, which is slightly soluble in light petroleum, and crystallises in large, transparent, well-developed, monosymmetric prisms, melting at 59—60°.

The acid obtained by boiling $\beta\gamma$-pentylenic acid, prepared from methylparaconic acid, with a 10 per cent. solution of soda has precisely the same properties, and forms the same additive products.

The three isomeric pentylenic acids and their dibromides are now all known in the pure state, and differ so greatly in properties as to be easily distinguished.

	B. p.	M. p. of dibromide.
$\alpha\beta$-Pentylenic acid, $CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$ (propylideneacetic acid)	201°	56°
$\beta\gamma$-Pentylenic acid, $CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$ (ethylidenepropionic acid)	194°	65°
$\gamma\delta$-Pentylenic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ (allylacetic acid)	187°	58°

The production of the $\beta\gamma$-acid, in addition to the $\alpha\beta$-derivative, by the condensation of propaldehyde with malonic acid, renders it probable that β-hydroxyvaleric acid is formed as an intermediate product, and then decomposes in the usual way, with formation of both isomerides. A. H.

Constitution of Dibromolevulinic acid. By L. Wolff (*Ber.* 26, 2216—2221; compare Abstr., 1891, 416).—Dibromolevulinic acid has been shown to have one of the two formulæ

$$CH_2Br{\cdot}CO{\cdot}CHBr{\cdot}CH_2{\cdot}COOH \text{ or } CH_3{\cdot}CO{\cdot}CBr_2{\cdot}CH_2{\cdot}COOH.$$

The oxidation of the acid by means of concentrated nitric acid proves that the former of these represents its constitution, the products formed being dibromodinitromethane and monobromosuccinic acid; oxalic acid and fumaric acid, both probably derived by a secondary reaction from the latter, being also produced. Dibromodinitromethane, $CBr_2(NO_2)_2$, has been previously obtained by Losanitsch (*Ber.*, **15**, 473; **16**, 51), by the oxidation of tribromaniline and ethylenic dibromide, in both of which compounds only one bromine atom is combined with a single carbon atom. It is a very volatile, faintly yellowish-green oil, which solidifies to white, lustrous plates, melting at 10°. It is somewhat soluble in water, more readily in dilute acids, and liberates iodine from solutions of potassium iodide and hydriodic acid. On treatment with caustic potash solution, it is converted into the explosive yellow potassium

salt, $CBrK(NO_2)_2$, described by Losanitsch; his statement that a solution of this salt, when decomposed by dilute sulphuric acid, yields the original dibromodinitromethane and not the monobromo-compound as might have been expected, has been confirmed. This reaction shows that monobromodinitromethane must be a very unstable substance, and throws some light on the formation of the dibromo-derivative by the oxidation of a group only containing one bromine atom.

In connection with the decomposition of dibromolevulinic acid by boiling with water, the constitution of tetric and pentic acids is being further investigated. The following results have already been obtained. On oxidation, tetric acid yields a considerable amount of diacetyl, so that this method might well be employed for the preparation of the latter. The acid is decomposed by water at 200°, among the volatile, neutral substances formed, being one which boils at 155—156°, and has the composition $C_4H_8O_2$; this substance shows all the properties of a ketonic or aldehydo-alcohol, and, on oxidation, yields propionic acid. Its formula is, probably, $COEt{\cdot}CH_2{\cdot}OH$.

Tetric acid is converted by the action of concentrated nitric acid, or, better, of nitrous acid, into a white, crystalline compound, a series of colour changes, such as occur in the formation of a pseudonitrole, taking place. This substance has the formula $C_5H_8O_3{\cdot}NO$, is very slightly soluble in the ordinary solvents, melts at 131° with decomposition, and gives Liebermann's reaction. It has no longer the character of an acid, and is decomposed by boiling water or alkalis. The compound may be either a nitroso-derivative or a salt of nitrous acid. A. H.

Action of Sodium Ethoxide and Ammonia on Isocaprolactone. By T. Ström (*J. pr. Chem.*, [2], **48**, 209—222).—Isocaprolactone is obtained in theoretical quantity by distilling terebic acid in an apparatus so arranged that for every drop of the distillate that runs into the receiver, 7—8 drops run back into the distilling flask. The distillate is then subjected to a second distillation.

Diisohexolactone, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CMe_2-O\end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix}CH_2{\cdot}CMe_2\\ |\\ CO-O\end{matrix}$, is obtained by heating sodium ethoxide with isacaprolactone dissolved in absolute alcohol on the water bath for eight hours. The product, which contains an acid, is dissolved in ether, and the acid extracted from the solution by shaking with aqueous potassium carbonate. It separates from ether in large, colourless crystals, and from alcohol in needles, melts at 103·8°, is volatile with steam, and is insoluble in cold sodium hydroxide, but slowly dissolves when heated. When heated with water, or with dilute hydrochloric or sulphuric acid, it is slowly converted into tetramethyloxetone.

Tetramethyloxetonecarboxylic acid (diisohexonic acid),

$$\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CMe_2-O\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH(COOH)\\ |\\ O\text{——}CMe_2\end{matrix}\!\!>\!CH_2,$$

is obtained, together with tetramethyloxetone, by boiling the preceding compound with dilute sodium hydroxide. It crystallises from ether in short, thick crystals, and from water in needles containing $\frac{1}{2}H_2O$, which melt at 81°. The anhydrous acid melts at 108°. When boiled with water or dilute acids, or when heated above its melting point, it is converted into tetramethyloxetone and carbonic anhydride. The *calcium salt*, $(C_{13}H_{19}O_4)_2Ca$, is more soluble in cold than in warm water, and crystallises from alcohol in small needles. The *barium salt* crystallises in needles, and is soluble in alcohol. The *silver salt* is obtained as a white, voluminous precipitate, is not very stable, and when boiled with water, decomposes into carbonic acid, tetramethyloxetone, and metallic silver.

Tetramethyloxetone, $C\left(<\begin{matrix}CH_2\cdot CH_2\\ O-CMe_2\end{matrix}\right)_2$, is best obtained by boiling the product of the action of sodium ethoxide on isocaprolactone with water, acidifying with hydrochloric acid, and subjecting the mixture to steam distillation. It is a colourless liquid, boils at 178·5°, has an odour resembling that of peppermint, and is more soluble in cold water than in water at 35—90°. It is not altered by dilute alkalis or acids, and slowly reduces ammoniacal silver solution.

γ-Hydroxyisocaproamide, $OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CONH_2$, is obtained by saturating a solution of isocaprolactone in absolute alcohol at 0° with dry ammonia, and heating the mixture for four hours in a sealed tube at 100°, or by shaking the lactone for 24 hours with an aqueous solution of ammonia saturated at 0°. It crystallises in large tablets or beautiful lustrous plates, and melts at 101°. It is not altered by cold sodium hydroxide, but, on heating, ammonia and sodium hydroxyisocapronate are formed. When heated with hydrochloric acid, the lactone and ammonium chloride are formed. When heated in a paraffin bath at 147°, it is decomposed into the lactone and ammonia.

Ammonium γ-hydroxyisocaproate is obtained by adding ammonium sulphate to a solution of barium γ-hydroxyisocaproate and evaporating the filtrate over sulphuric acid. It crystallises from absolute alcohol with partial decomposition, melts at 127°, and at higher temperatures is converted into the lactone, ammonia, and water.

E. C. R.

Aticonic acids, New Isomerides of the Itaconic, Citraconic, and Mesaconic acids. By R. Fittig (*Ber.*, **26**, 2082—2083).—In a previous paper (this vol., i, 189), the author stated that the homologues of itaconic acid are scarcely altered by the action of boiling aqueous soda, only small quantities of readily soluble acids, which were taken for hydroxy-acids, being formed. Further investigation has, however, shown that these soluble acids are, in reality, new isomerides of the itaconic acids, and the name of *aticonic acids* has, therefore, been given to them. The new acids corresponding with dimethylitaconic, hexylitaconic, and phenylitaconic acids have all been prepared. They seem to bear the same relation to the itaconic acids that the citraconic acids do to the mesaconic acids. Thus, a solution of phenylaticonic acid in chloroform, on treatment with a few drops of a dilute solution of bromine in the same solvent, at once deposits crystals of pure phenylitaconic acid.

The aticonic acids differ from the itaconic and mesaconic acids by being readily soluble in water, whilst they are distinguished from the citraconic acids by not being volatile with steam; their barium and calcium salts are, moreover, much less soluble in water than those of the mesaconic acids. The melting points of the aticonic acids are higher than those of the citraconic, but lower than those of the itaconic and mesaconic acids, as is shown by the following table.

	Dimethyl-.	Hexyl-.	Phenyl-.
Mesaconic acid ..	185—186°	153—154°	210°
Itaconic acid	162—163	129—130	180
Aticonic acid....	about 140°	about 110°	148
Citraconic acid ..	91—93°	86°	103—106°

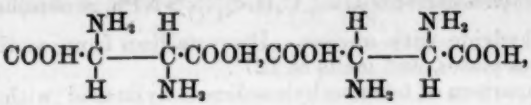
On reduction with sodium amalgam, phenylaticonic acid is converted into the same benzylsuccinic acid as is given by the three other isomerides. A. H.

Isomeric Diamidosuccinic acids. By J. M. Farchy and J. Tafel (*Ber.*, **26**, 1980—1990).—Tafel has shown (Abstr., 1887, 468) that Lehrfeld's diamidosuccinic acid is obtained by the reduction of dihydroxytartaric osazone. On repeating the reduction experiment under the conditions described below, the authors isolated the diamidosuccinic acid previously described (*loc. cit.*), together with an isomeride; the experiments to be described show that the former is the meso-modification and the latter the racemic modification.

Dihydroxytartaric osazone (100 grams) is dissolved in a solution of sodium hydroxide (25 grams) in water (600 c.c.) at 0°, to which 1 kilo. of ice is added; 2½ per cent. sodium amalgam (3 kilos.) is then introduced in large portions at a time within five minutes, the mixture being agitated meanwhile and for half an hour subsequently, after which, 30 per cent. sulphuric acid (167 grams) is added slowly, the temperature rising to 40°. The mixture is shaken for an hour, cooled, and extracted with ether; the alkaline liquid is then acidified with dilute sulphuric acid, and the flocculent precipitate (16 grams) which separates, after 24 hours, is collected and washed with hot alcohol; it consists of crude mesodiamidosuccinic acid. The mother liquor is neutralised and shaken with ether, when, after several days, a crystalline precipitate (10 grams) of crude racemic diamidosuccinic acid separates.

Mesodiamidosuccinic acid, $COOH\cdot\overset{NH_2}{\overset{|}{C}}\overset{H}{\overset{|}{}}\!\!-\!\!-\overset{NH_2}{\overset{|}{C}}\overset{H}{\overset{|}{}}\cdot COOH$, has been already described (*loc. cit.*). The *copper* salt is a blue precipitate containing 1 mol. H_2O; the *diacetyl* derivative, $C_2H_2(NHAc)_2(COOH)_2$, decomposes at 235°; and the *dibenzoyl* derivative melts at 213° with decomposition. If a neutral solution of the sodium salt, mixed with a dilute solution of sodium nitrite (2 mols.), is gradually added to dilute hydrochloric acid containing hydrogen chloride (5 mols.), mesotartaric acid is formed; its isolation is described in detail.

Racemic diamidosuccinic acid,



is purified by crystallising the crude acid from 2 per cent. hydrochloric acid; it crystallises in colourless prisms with $1H_2O$, and exhibits the same general properties as the meso-modification, but differs from it in the following respects:—It is less soluble in hot water, and more soluble in dilute ammonia; when heated, it decomposes.

The *copper* salt forms deep blue, hydrated leaflets, and is insoluble in water; the *diacetyl* derivative decomposes at 235°, and the *dibenzoyl* derivative melts at 182°. The acid is converted into racemic acid when treated with dilute nitrous acid. A. R. L.

Anhydride Formation in the case of Substituted Succinic acids. By E. Hjelt (*Ber.*, **26**, 1925—1928).—The acids were heated for a given time at a given temperature, and the amount of anhydride formed calculated from the observed loss of weight. The percentage of acid converted into anhydride increases in the following series, and, when the heating is continued for one hour at 160°, is expressed by the numbers in brackets: succinic acid, phenyl-, methyl- (14·1), ethyl- (14·5), propyl- (16·6), isopropyl- (29·6), and unsymmetrical dimethyl- (36·7) succinic acids, phthalic acid. The different radicles are found to exert here much the same influence as on the lactone formation in the case of γ-hydroxy-acids (Abstr., 1891, 822). C. F. B.

Tetramethylene Derivatives. By W. H. Perkin, Jun. (*Ber.*, **26**, 2243—2244; compare Trans., 1887, 18).—The author has previously shown that ethylenic bromide reacts with ethylic sodiomalonate to form ethylic trimethylenedicarboxylate, together with about 3 per cent. of ethylic butanetetracarboxylate,

$$CH(COOEt)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2.$$

If, however, ethylenic chloride be substituted for the bromide, the yield of this second substance rises to about 30 per cent. The derivatives of this substance and of tetramethylenedicarboxylic acid, which can be easily prepared from it, are therefore being submitted to a renewed investigation.

Tetramethylenetetracarboxylic acid crystallises from water with $2H_2O$ in thick prisms, which melt at 198—203°, with decomposition into carbonic anhydride and tetramethylenedicarboxylic acid. The temperature of decomposition, which was formerly stated as 145—150°, is considerably lowered by small amounts of impurity.

Tetramethylenedicarboxylic acid melts at 137—138° (formerly stated as 130°). The *dimethylic salt* boils at 222—223°. On boiling with acetic chloride, the acid is converted into the anhydride, $C_4H_6{<}^{CO}_{CO}{>}O$ which melts at 75° and boils at 270—273° without decomposition.

Tetramethylenedicarboxyanil, $C_4H_8<\begin{matrix}CO\\CO\end{matrix}>NPh$, is obtained by heating the anhydride with aniline. It crystallises from methyl alcohol in colourless plates, and melts at 127°.

The comparison of tetramethylenedicarboxylic acid with camphoric acid, which is now looked on by many chemists as isopropylmethyltetramethylenecarboxylic acid, $\begin{matrix}CH_2\cdot CMe\cdot COOH\\|\\CH_2\cdot CPr^{\beta}\cdot COOH\end{matrix}$, is also being prosecuted. On heating with sulphuric acid, the latter yields carbonic oxide and is converted into sulphocamphoric acid, whilst tetramethylenedicarboxylic acid is simply converted into the anhydride, no gas being evolved.

Many attempts have been made to ascertain whether tetramethylenedicarboxylic acid and the corresponding pentamethylenedicarboxylic acid, like the hexahydrophthalic acid to which they are closely allied in structure, occur in two isomeric forms (cis and trans), but hitherto with negative results.

Tetramethylenedicarboxylic anhydride is converted by the action of bromine and phosphorus into a substance which, when treated with water, yields *dibromotetramethylenedicarboxylic acid*, $\begin{matrix}CH_2\cdot CBr\cdot COOH\\|\\CH_2\cdot CBr\cdot COOH\end{matrix}$. This acid crystallises from water in lustrous plates melting at 198—203°. On boiling with alkalis, it loses hydrogen bromide and forms an unsaturated acid, $\begin{matrix}CH:CH\\|\\CH_2\cdot CBr\cdot COOH\end{matrix}$, which crystallises from water in needles melting at 122°. The *barium salt* crystallises in plates, and, after drying in a vacuum, has the formula $(C_5H_4BrO_2)_2Ba$. When treated with bromine vapour, the acid takes up a molecule of bromine, forming the acid $C_5H_5Br_3O_2$, which is probably *tribromotetramethylenecarboxylic* acid. The study of this substance is being continued in the hope of preparing from it the unsaturated acid, $\begin{matrix}CH:CH\\|\\CH:C\cdot COOH\end{matrix}$, the relation of which to benzene makes it a subject of great interest.

The details of these researches will be subsequently published.

A. H.

Synthesis of Pentamethylenecarboxylic acid. Hexamethylenecarboxylic (Hexahydrobenzoic) acid and Azelaic acid. By E. Haworth and W. H. Perkin, Jun. (*Ber.*, **26**, 2246—2250).—Pentamethylenic dibromide, prepared according to Gustavson and Demyanoff's method from pentamethylenediamine (*J. pr. Chem.*, [2], **39**, 542), probably contains at least 60 per cent. of tetramethylenic dibromide.

By the action of ethylic sodiomalonate on this mixture of bromides, a product is obtained which can be separated by fractional distillation into two portions, one boiling at 240—250° under 760 mm. pressure, and the other at 270—275° under 50 mm. pressure. By hydrolysis of the first fraction, pentamethylenedicarboxylic acid is obtained, together with hexamethylenedicarboxylic acid.

Pentamethylenedicarboxylic acid, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>C(COOH)_2$, melts at 185°, is indifferent to soda at ordinary temperatures, and, on distillation, yields carbonic anhydride and *pentamethylenecarboxylic acid*, $C_5H_9\cdot COOH$. The latter is a colourless oil, boils at 214—215°, and is not oxidised by permanganate; it seems to be identical with Wislicenus and Gärtner's pentamethenecarboxylic acid (*Annalen*, 275, 339).

Hexahydrobenzoic (hexamethylenecarboxylic) acid is obtained by evaporating the mother liquors of the pentamethylenedicarboxylic acid on the water bath and distilling the residue. It is a colourless oil, boils at 231—233°, and solidifies when cooled.

The distillate mentioned above, as boiling at 270—275° under 50 mm. pressure, consists of ethylic heptanetetracarboxylate, and when hydrolysed and heated at 220°, yields azelaic acid.

The authors failed to obtain heptane derivatives by the action of bromine on the disodium derivative of ethylic heptanetetracarboxylate. The product contained azelaic acid. E. C. R.

Acrylamide. By Moureu (*Bull. Soc. Chim.*, [3], **9**, 417—419).—Acrylamide is prepared by saturating a cooled benzene solution of acrylic chloride with dry ammonia. The solution, filtered from ammonium chloride and cooled, deposits thin, bright leaflets melting at 84—85°, and of a nacreous lustre in mass. Acrylamide is inodorous and easily soluble in water, alcohol, ether, chloroform, and most of the usual solvents. It melts sharply at 84—85°, gives off ammonia at 125°, and solidifies suddenly between 150° and 155°; the product is almost of the same weight as the acrylamide taken. It is a tough, horny mass, non-crystalline, insoluble in all the usual neutral solvents, and has a bright, resinous fracture. Hydrochloric and acetic acids and alkaline solutions are without action on it, even after prolonged boiling. It appears to be a polymeride of very high molecular weight.

Acrylamide decomposes when heated above 155°: rapidly at 190—200°.

It readily forms an additive compound with bromine in the cold, small crystals of $\alpha\beta$-dibromopropionamide being formed, soluble in chloroform, and melting at 130—133°. A small quantity of a more brominated derivative is formed at the same time, which cannot be entirely eliminated by crystallisation. W. T.

Substituted Acrylamides. By Moureu (*Bull. Soc. Chim.*, [3], **9**, 419—424).—The substances described do not polymerise, like acrylamide, when heated.

Methylacrylamide is a colourless liquid with a feeble odour of acetamide. It distils between 126° and 129° under a pressure of 30 mm., and under atmospheric pressure at 220° with partial decomposition. Its sp. gr., at 0°, is 1·018.

Ethylacrylamide closely resembles the methyl derivative, and distils at the same temperatures under similar conditions; sp. gr. = 0·978 at 0°.

Phenylacrylamide is obtained by the same process as the preceding compounds. It is a white, well-crystallised compound, soluble in boiling water, alcohol, and chloroform, but less soluble in benzene. It melts at 104—105°, begins to decompose at 275°, and the decomposition proceeds rapidly at 300°. No quinoline is produced even in presence of sulphuric acid, phosphoric anhydride, or zinc chloride.

Paratolylacrylamide forms fine, white, nacreous crystals melting at 141°.

Orthotolylacrylamide is a well crystallised substance melting at 109—110°.

Methylphenylacrylamide forms crystals melting at 76—77·5°.

Orthohydroxyphenylacrylamide melts at 123—124°. It is soluble in cold alkalis, hence the phenolic function is not affected during its formation. W. T.

Preparation of Carbamide. By A. Reychler (*Bull. Soc. Chim.*, [3], **9**, 427—429).—A dilute solution of sodium hypochlorite is gradually added to an aqueous solution of potassium cyanide; after the odour of cyanogen compounds has disappeared, an excess of ammonium sulphate is added, the whole heated to the boiling point, and then evaporated to dryness. The residue is extracted with 94 per cent. alcohol, and yields a crude product containing 89·4 per cent. of the theoretical quantity of carbamide.

If sodium peroxide is used as the oxidising agent, the yield is only 1·5 grams of carbamide from 10 grams of cyanide. Formamide yields 37·5 per cent. of the calculated amount of carbamide when oxidised by sodium hypochlorite in presence of sodium carbonate and treated as above; no carbamide is obtained, however, if sodium peroxide is substituted for hypochlorite. W. T.

Action of Thionyl Chloride on Alkyl Carbamates. By G. Schroeter and M. Lewinski (*Ber.*, **26**, 2171—2174).—Thionyl chloride in benzene solution withdraws the elements of alcohol from 2 mols. of an alkyl carbamate, $NH_2{\cdot}COOR$, and an allophanate, $NH_2{\cdot}CO{\cdot}NH{\cdot}COOR$, is formed; other acid chlorides do not exercise this influence. This reaction was carried out in the cases R = Me, and = C_5H_{11}; the yield is a good one, respectively 70 and 50—55 per cent. of the theoretical, and the method is, consequently, well adapted for the preparation of allophanates. Contrary to expectation, cyanuric acid is not formed in the reaction; it is, however, if the substances are heated together in xylene solution at 150° in a sealed tube. C. F. B.

Iodoso- and Iodoxy-derivatives of Benzene. By C. Willgerodt (*Ber.*, **26**, 1947—1950).—The *chloriodides* $C_6H_4Cl{\cdot}ICl_2$ [1 : 2, 1 : 3, and 1 : 4] and $C_6H_4Br{\cdot}ICl_2$ [1 : 3] were prepared by chlorinating the corresponding iodides; they are yellow, crystalline substances, and decompose respectively at 95—98°, 100°, 116—117°, and 104°. When treated with dilute aqueous soda, they yield the corresponding *iodoso-compounds* $C_6H_4Cl{\cdot}IO$, &c.; these are yellow, amorphous sub-

stances, and decompose at 85°, the first with explosion; when dissolved in acetic acid, they yield *acetyl derivatives*, $C_6H_4Cl{\cdot}I(OAc)_2$, &c., as colourless or white crystals melting respectively at 140°, 154—155°, 185—190° (with decomposition), and 163—164°. When the iodoso-compounds are heated on a watch-glass, or boiled with water, they decompose into iodides and *iodoxy-compounds*, $C_6H_4Cl{\cdot}IO_2$, &c.; these crystallise in white or colourless, hexagonal plates, and explode respectively at 203°, 233°, 243°, and 230°. C. F. B.

Action of Alkalis on Paranitrotoluene and on Paranitrotoluenesulphonic acid. By O. Fischer and E. Hepp (*Ber.*, **26**, 2231—2234).—Paranitrotoluene, when acted on by alkalis, yields a red, amorphous substance (Klinger, *Ber.*, **16**, 941), which may perhaps be azoxystilbene (*Ber.*, **19**, 3234). Paranitrotoluenesulphonic acid, in the same manner, yields the dyes "sun-yellow," "Mikado-brown," and "Mikado-orange." The authors have found that when paranitrotoluene is brought into a strong solution of caustic soda in methyl alcohol, and the mixture gently heated, an insoluble yellow mass is formed. This consists mainly of dinitrosostilbene, accompanied by smaller amounts of paradinitrodibenzyl and paradinitrostilbene, which may be extracted by alcohol and xylene respectively.

The *dinitrosostilbene*, $C_{14}H_{10}N_2O_2$, the constitution of which is not yet known, is insoluble in xylene, but may be recrystallised from ethylic benzoate or ethylic acetoacetate. It forms orange-yellow, round, crystalline nodules melting at 263°, and yields a cherry-red solution in concentrated sulphuric acid, but is insoluble in dilute acids or alkalis. On reduction, it is converted into paradiamidostilbene. When paranitrotoluene is treated with a less concentrated solution of caustic soda, the red, amorphous substance already referred to is obtained, and it is also formed when dinitrodibenzyl is submitted to the same treatment.

Paranitrotolueneorthosulphonic acid is converted, by the action of concentrated aqueous soda, into *disodium dinitrosostilbenedisulphonate*; it separates from alcohol in compact, reddish crystals, and gives with barium chloride an orange-yellow precipitate of the corresponding *barium* salt. Dinitrosostilbenedisulphonic acid is converted by oxidation into dinitrostilbenedisulphonic acid, and by energetic reduction into diamidostilbenedisulphonic acid. Moderate reduction, on the other hand, yields colouring matters of redder shade, which are probably azoxy- and azo-derivatives. When paranitrotoluenesulphonic acid is treated with more dilute aqueous soda, the colouring matters known as "sun-yellows" are formed, and these do not yield dinitrosostilbenedisulphonic acid on recrystallisation. A. H.

Synthesis of Phenols from Ethylic Acetoacetate. By E. Knoevenagel (*Ber.*, **26**, 1951—1952).—By the condensation of ethylic acetoacetate with aldehydes, substances were obtained (this vol., i, 419) which are derivatives of (1) (see next page); these form dibromo-additive compounds, which, when heated on the water bath, lose hydrogen bromide and yield phenols:

(1) $CH<\begin{matrix}CH\cdot CH_2\\CO\cdot CH_2\end{matrix}>CH_2 \rightarrow CH<\begin{matrix}CH\text{——}CH\\C(OH):CH\end{matrix}>CH.$

In this way, 3-methyl-Δ_2-ketohexene yields 1 : 3-cresol, and 3 : 5-dimethyl-Δ_2-ketohexene yields 1 : 3 : 5-xylenol. C. F. B.

Action of Chlorine on Catechol and Orthamidphenol. By T. Zincke and F. Küster (*Ber.*, **26**, 2104—2117; compare Abstr., 1890, 1255).—By the action of alkalis on $\gamma\gamma$-hexachloroketopentene (m. p. 92°) at 40—50°, a bibasic acid, $C_5Cl_4H_2O_4$, is formed, and is being further investigated. It has already been shown (Abstr., 1890, 754) that, on treating the ketone with alkali at 0°, an unstable acid is formed which is isomeric with that (m. p. 127°) from the $\beta\gamma$-ketone; it appears to be pentachlorobutenecarboxylic acid $CCl_2:C:CCl\cdot CCl_2\cdot COOH$, crystallises from light petroleum, and melts at 97—98°. The acid is soluble in water at ordinary temperatures; on warming, a turbidity is produced, and carbonic anhydride evolved (see below). The *sodium salt*, $C_4Cl_5\cdot COONa$, crystallises in silvery, lustrous plates. The $\gamma\gamma$-ketone, C_5Cl_5BrO, is decomposed by the action of soda at 0° in a similar manner to the pentachloro-ketone, and yields a corresponding acid, $C_4Cl_4Br\cdot COOH$, which is deposited in microscopic prisms; it melts at 100—100·5°, resolidifies, and melts again at 114°; on crystallisation from light petroleum, long, colourless needles are obtained; from ether and light petroleum, compact, granular crystals; both forms melt at 110°. On heating with water, it undergoes a similar decomposition to the pentachloro-acid, but the product, which is an oil, volatile with steam, has not been isolated. *Pentachlorobutidene* (or *-butine*), C_4Cl_5H, is prepared by boiling the pentachloro-acid with water; on distilling the product with steam, it passes over as a colourless oil with a characteristic, penetrating odour, and boils at 125° under 75—80 mm. pressure. The compound is extremely stable, and does not combine with bromine; attempts to eliminate hydrogen chloride were unsuccessful; it may be represented by the formula $CCl_2:C:CCl\cdot CHCl_2$ or $CCl_2\cdot C:C\cdot CHCl_2$. In addition to the preceding substance, a solid was obtained by the decomposition of the acid; it is not volatile with steam, and has not been investigated.

It has already been shown that, on reduction, the above pentachloro-acid yields an acid of the formula $C_5H_8O_2$; with proper precautions, which are fully described in the paper, the yield is 30—35 per cent. of the theoretical; the same compound is obtained from the bromo-acid $C_4Cl_4Br\cdot COOH$, and also from that derived from the $\beta\gamma$-ketone (m. p. 32°); the fact that this acid readily combines with hydrogen bromide, and that the product only yields traces of valerolactone, caused it to be regarded as propylideneacetic acid; Viefhaus has recently shown (this vol., i, 392) that the compound, termed by Ott propylideneacetic acid, contained ethylidenepropionic acid, and, on comparison, it is found that the above acid, $C_4H_7\cdot COOH$, and ethylidenepropionic acid yield identical salts and oxidation products. This conclusion is not in harmony with the observations of Fittig and Fränkel, who state that ethylidenepropi-

onic acid is readily converted into valerolactone (*Annalen*, **255**, 27). The barium salt, insoluble in alcohol, described by Ott (Abstr., 1891, 1453) as dissolving more readily in cold water than in hot, crystallises from hot water on cooling the solution. J. B. T.

Dinitrocatechol and its Conversion into Nitranilic acid. By R. Nietzki and F. Moll (*Ber.*, **26**, 2182—2184).—When diacetylcatechol is dissolved in pure nitric acid at 0°, a *dinitro-derivative* is obtained in yellow needles melting at 124°; this, on hydrolysis, yields *dinitrocatechol* [$(OH)_2:(NO_2)_2 = 1:2:3:5$ probably], crystallising in yellow needles, and melting at 164°. When this is dissolved in a mixture of nitric and sulphuric acids, it is converted into nitranilic acid, and this is shown to be identical with the "dinitrodioxyquinone" obtained by Gruber (Abstr., 1879, 644) by the action of nitrous acid on protocatechuic acid; Gruber's compound is not, therefore, a chemical individual. Dinitrocatechol, or, better, its diacetyl derivative, when reduced with stannous chloride, yields *diamidocatechol*; the *hydrochloride*, with 2HCl, was prepared; the free base oxidises rapidly in the air with formation of steel-blue needles of a compound $C_6H_2(NH)_2(OH)_2$. The base does not react with orthodiketones, and is consequently not an orthodiamine.

C. F. B.

Derivatives of Phloroglucinol. By R. Nietzki and F. Moll (*Ber.*, **26**, 2185—2187).—Pure nitric acid at 0° converts triacetylphloroglucinol into a nitro-derivative, which, when treated with potash, yields the potassium salt of trinitrophloroglucinol. This, when reduced with stannous chloride, yields *triamidophloroglucinol*, the *hydrochloride* of which, with 2HCl, forms colourless needles turning brown in the air. The base itself is oxidised by manganese dioxide in alkaline solution to croconic acid.

When the potassium salt of trinitrosophloroglucinol is heated at 100° with aqueous ammonia in a sealed tube, a compound,

$$NOH{:}C_6O_2(NOK)_2{:}NH,$$

is formed; if the phenol is itself used, instead of its potassium salt, the product has the composition $C_6O(NOH)_3(NH)_2 + NH_3$.

C. F. B.

Parachlororthotoluidine. By A. Claus (*Annalen*, **276**, 347—349).—Claus and Stapelberg have stated (this vol., i, 580) that parachlororthotoluidine melts at 16°; the author finds that when the base having the last-mentioned melting point is thrice rapidly distilled over a free flame, a white, crystalline preparation is obtained; this, when crystallised from alcohol, melts at 29—30°, which value agrees with that obtained by other observers. A. R. L.

Action of Ethylenediamine on Nitrophenols, their Ethers and corresponding Halogen Derivatives. By K. Jedlicka (*J. pr. Chem.* [2], **48**, 193—208).—Orthonitrophenol and ethylenediamine, when heated together in a sealed tube at 180—190° for 10 hours,

yield tarry products, from which no definite compound can be isolated. When heated at 170°, scarcely any action takes place.

Diorthonitrodiphenylethylenediamine, $C_2H_4(NH\cdot C_6H_4\cdot NO_2)_2$, is obtained by heating orthonitranisoïl with ethylenediamine at 180° in a sealed tube. The yield is 20 per cent. on the weight of the nitranisoïl. A yield of 16 per cent. is obtained by heating orthobromonitrobenzene with ethylenediamine at 120—130°. Diorthonitrodiphenylethylenediamine crystallises from benzene in small, interlacing, orange-red needles, melts at 190°, and decomposes at a higher temperature. It is a weak base, dissolves in concentrated mineral acids, and is precipitated in orange-yellow flocks on the addition of water. The *diacetyl derivative* crystallises in small, transparent, pale yellow prisms, and melts at 215—216°. The *dibenzoyl derivative* separates from solution in oily drops which solidify after a time, and then melts at 218—220°.

Diorthonitrodiphenylethylenediamine cannot be obtained by heating a mixture of orthonitraniline and ethylenic bromide. At 150°, scarcely any action takes place, and at higher temperatures dark, uninviting products are obtained.

A yield of 40—50 per cent. of orthobromonitrobenzene is obtained when bromobenzene is treated with concentrated nitric acid at a temperature not exceeding −10°. At −40—50° no action takes place.

Diparanitrodiphenylethylenediamine is obtained in small quantities by heating paranitrophenol and ethylenediamine for some hours at 160—170°, and then for six hours at 190—200°. A 14 per cent. yield is obtained by heating paranitranisoïl with ethylenediamine at 160—170°; and a 30 per cent. yield is obtained in a similar way from parabromonitrobenzene at 130°. It crystallises from nitrobenzene in yellowish-brown microscopic needles, melts at 216°, has no basic properties, but dissolves in concentrated mineral acids, and is reprecipitated by the addition of water.

Tetranitrodiphenylethylenediamine cannot be prepared from orthoparadinitrophenol and ethylenediamine. A yield of 25 per cent. is obtained when methoxydinitrobenzene is employed, and an almost theoretical yield is obtained from bromodinitrobenzene. It crystallises in small, yellow, angular aggregates, melts at 302—303°, and is indifferent to alkalis and acids.

Tetranitroditertiarybutyldiphenylethylenediamine,

$$C_2H_4[NH\cdot C_6H_2(NO_2)_2\cdot C_4H_9]_2,$$

cannot be obtained from dinitrotertiarybutylphenol (m. p. 93°). A yield of 50—60 per cent. is, however, obtained from methoxydinitrobutylbenzene (m. p. 102°) by heating on the water bath or in a sealed tube at 120—130° for three hours. It crystallises in beautiful, small, sulphur-yellow needles, melts at 174—175°, and has no basic properties.

Hexanitrodiphenylethylenediamine cannot be obtained from picric acid. A yield of 70 per cent. is obtained by adding ethylenediamine to an alcoholic solution of methylic picrate, and warming the mixture on the water bath. It is also easily obtained by adding ethylenediamine to an alcoholic solution of picryl chloride, when much heat is

developed. It crystallises from nitrobenzene in beautiful, small, lemon-yellow leaflets, melts at 230°, decomposes at a higher temperature, and gives brownish-red solutions in aqueous alkalis. When heated with aqueous alkalis, it yields ethylenediamine and alkali picrate. It dissolves in concentrated sulphuric acid in the cold, and is precipitated by water in pale yellow flocks. When heated with sulphuric acid, it yields picric acid. E. C. R.

Molecular Weight of the Carbodiimides. By C. SCHALL (*Zeit. physikal. Chem.*, **12**, 145—154).—Four modifications of carbophenydiimide which the author has investigated give numbers for the elevation of the boiling point of acetone and ethylic acetate which correspond with the normal molecule $C(NC_6H_5)_2$. The numbers obtained from the depression of the freezing point of benzene indicate double and even triple molecules. The molecular weight of the carbodiparatolylimides was found to be always somewhat higher than that corresponding with the formula $C(NC_7H_7)_2$. J. W.

Introduction of the Phenyl Group into Cycloïd Compounds. By R. MÖHLAU and R. BERGER (*Ber.*, **26**, 1994—2004).—Diazobenzene chloride reacts with benzene in presence of synthetic aluminium chloride (this vol., i, 161), forming chlorobenzene and diphenyl. When diazobenzene chloride is mixed with a little toluene, and a mixture of warm toluene and aluminium chloride gradually added with shaking, the whole being finally heated to boiling, chlorobenzene and a mixture consisting of para- and perhaps ortho-methylphenylbenzene are obtained. The diazochlorides of ortho- and para-toluene, on treatment with either benzene or toluene, yield the corresponding chlorotoluenes. Diazobenzene chloride and diphenyl, in presence of aluminium chloride, yield chlorobenzene, paradiphenylbenzene (m. p. 204°), and isodiphenylbenzene (Schulze, *Annalen*, **174**, 233; **203**, 129).

For the action of diazobenzene chloride on naphthalene see this vol., i, 522.

β-Diazonaphthalene chloride and benzene react in presence of aluminium chloride, forming β-chloronaphthalene (m. p. 57—58°). A *phenylthiophen* is obtained by the action of diazobenzene chloride on thiophen in presence of aluminium chloride; it forms silvery leaflets, melts at 56—57°, and boils at 254°. It thus differs from α-phenylthiophen (Knes and Paal, Abstr., 1887, 238), and is probably the β-modification. Diazobenzene chloride reacts very energetically with pyridine, forming a mixture of 1-phenylpyridine and 3-phenylpyridine; it also reacts with equal energy with quinoline, forming 1-phenylquinoline. A. R. L.

Reaction of Hydrazine Hydrate with the Nitro-, Nitroso-, and Isonitroso-groups. By R. v. ROTHENBURG (*Ber.*, **26**, 2060—2061).—The preliminary experiments of the author show that the isonitroso-group (acetoxime, benzaldoxime) is removed by the action of an excess of hydrazine hydrate and replaced by the hydrazo-group $(NH_2{\cdot}N)''$. The nitroso- and nitro-groups, on the other hand (nitro-

benzene, paranitrosodimethylaniline, diphenylnitrosamine), are reduced to the amido-group. A. H.

Thionylbenzylhydroxylamine and Dibenzoxycarbamide. By A. MICHAELIS and G. SCHRÖTER (*Ber.*, **26**, 2155—2157.)—When an ethereal solution of thionyl chloride is added drop by drop to an ethereal solution of α-benzylhydroxylamine, the hydrochloride of the latter separates, and *thionylbenzylhydroxylamine*, OBz·N:SO, remains in the solution, and may be purified, after the ether has been driven off, by distillation under reduced pressure. It is a yellowish liquid, boiling at 153—154° under 50 mm. pressure, is decomposed by soda into sulphurous anhydride and benzylhydroxylamine, yields thionylphenylhydrazone, $NHPh·N:SO_2$, with phenylhydrazine acetate, and in the presence of moisture forms *benzylhydroxylamine benzylthiohydroxylamate*, $OBz·NH·SO_2·NH_3·OBz$, which crystallises in white plates, melts with decomposition at 84—85°, and with benzaldehyde yields sulphurous anhydride and α-benzylbenzaldoxime.

When a toluene solution of carbonyl chloride is added to a benzene solution of α-benzylhydroxylamine, *dibenzoxycarbamide*, $CO(NH·OBz)_2$, is formed; it crystallises in minute needles which melt at 88°.

C. F. B.

Thionylamines of Unsaturated Bases. Thionylphenylpropylamine. By A. MICHAELIS and W. JACOBI (*Ber.*, **26**, 2158—2162).—Allylamine does not yield a thionylamine with thionyl chloride, but butenylmethylmethylamine (butallylmethylcarbinamine), in which the double bond is farther removed from the amido-group, does yield *methylbutenylmethylthionylamine* (*butallylmethylcarbinthionylamine*), $CH_2:CH·CH_2·CH_2·CHMe·N:SO$, when treated in ethereal solution with thionyl chloride. This thionylamine is a colourless liquid which boils at 156—158°, and has sp. gr. 0·9986 at 15°; it is decomposed by alkalis.

Phenylpropylamine, prepared by reducing the phenylhydrazone of cinnamaldehyde (compare Tafel, Abstr., 1886, 940), is a colourless liquid which boils at 216—218°, and has sp. gr. = 0·951 at 15°; it forms a pale-yellow *platinochloride*, $2C_9H_{13}N,H_2PtCl_6$, which melts with decomposition at 233°; and, with phenylthiocarbimide, it yields *phenylpropylphenylthiocarbamide*, $CH_2Ph·CH_2·CH_2·NH·CS·NHPh$, melting at 95—96°. When its hydrochloride is heated with a benzene solution of thionyl chloride, *phenylpropylthionylamine*,

$$CH_2Ph·CH_2·CH_2·N:SO,$$

is formed; this is a brownish-yellow liquid, which is decomposed by alkalis or on heating. With sulphurous acid in ethereal solution, phenylpropylamine yields *phenylpropylthionamic acid*,

$$CH_2Ph·CH_2·CH_2·NH·SO_2H,$$

a white, amorphous powder, which with phenylpropylamine yields lustrous crystals of *phenylpropylamine phenylpropylthionamate*, $CH_2Ph·CH_2·CH_2·NH·SO_2·NH_3·CH_2·CH_2·CH_2Ph$, decomposing at 290°, and with benzaldehyde quadratic plates of *benzaldehyde phenyl-*

propylthionamate, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}N(SO_2H){\cdot}CHPh{\cdot}OH$, melting at 105—106°. C. F. B.

Action of Thionyl Chloride on Benzylamine and its Homologues; some Derivatives of the latter. By A. MICHAELIS, G. SCHRÖTER, and E. LINOW (*Ber.*, **26**, 2162—2171).—The action of thionylaniline on benzylamine (compare this vol., i, 515) gives rise to benzylideneaniline, free sulphur, probably ammonia, and, in addition, ammonium thiosulphamate and trithionamate; these last two substances dissolve in water, yielding respectively ammonium thiosulphate and trithionate. *Ammonium trithionate* has not hitherto been prepared; it forms anhydrous prismatic crystals.

The action of thionyl chloride on the homologues of benzylamine was also studied. With the tolylmethylamines, $C_6H_4Me{\cdot}CH_2{\cdot}NH_2$, it forms thionyltolylmethylamines, which yield aldehydes when heated. With derivatives of the type $Ph{\cdot}[CH_2]_n{\cdot}NH_2$ [$n > 1$], thionylamines are formed, which yield no aldehydes. With derivatives of the type $CHRPh{\cdot}NH_2$ [R = Me or Ph], thionylamines are formed which, at a comparatively high temperature, yield ketones. Thiocarbamides were prepared from the amines by the addition of carbon bisulphide; whilst the action of sulphurous anhydride on the amines gave rise to thionamic acids, the amine salts and benzylidene derivatives of which were also prepared. The *thionyltolylmethylamines*, $C_6H_4Me{\cdot}CH_2{\cdot}N{:}SO$ [1 : 2, 1 : 3, and 1 : 4], are light-brown liquids, which yield aldehydes when heated.

Thionyl-β-phenylethylamine, $CH_2Ph{\cdot}CH_2{\cdot}N{:}SO$, is a yellow liquid, boiling at 170—173° under 25 mm. pressure; *β-phenylethylthionamic acid*, $CH_2Ph{\cdot}CH_2{\cdot}NH{\cdot}SO_2H$, is a white, amorphous powder, which sublimes without melting, and yields a *β-phenylethylamine salt*, crystallising in rhombic prisms, which also sublime without melting, and a *benzaldehyde derivative*, $CH_2Ph{\cdot}CH_2{\cdot}N(SO_2H){\cdot}CHPh{\cdot}OH$, in white crystals melting at 114°; *acetyl-* and *benzoyl-β-phenylethylamine*, $CH_2Ph{\cdot}CH_2{\cdot}NHBz$, melt at 51° and 116° respectively; *phenyl-β-phenylethylcarbamide*, $CH_2Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh$, melts at 106°; the *picrate* of β-phenylethylamine at 168°. *Thionyl-α-phenylethylamine*, $CHMePh{\cdot}N{:}SO$, is a brownish-yellow liquid, and yields acetophenone when heated; *α-phenylethylthionamic acid*, $CHMePh{\cdot}NH{\cdot}SO_2H$, resembles the corresponding β-compound, but does not yield a benzaldehyde derivative; *phenyl-α-phenylethylcarbamide*,

$$CHMePh{\cdot}NH{\cdot}CS{\cdot}NHPh,$$

forms silky crystals melting at 106°; *di-α-phenylethylthiocarbamide*, $CS(NH{\cdot}CHMePh)_2$, melts at 163°; *α-phenylethylamine α-phenylethylthiocarbamate* melts at 143°; the *picrate* at 189°.

Thionylbenzhydrylamine, $CHPh_2{\cdot}N{:}SO$, is a light yellow liquid, which boils at 88° under 35 mm. pressure, and yields benzophenone when heated under atmospheric pressure; *benzhydrylamine* sulphate melts at 244°; the *acetate* at 141°; with benzaldehyde, the amine yields a *benzylidene* compound, $CHPh_2{\cdot}N{:}CHPh$, melting at 98—99°, and in a similar way *orthohydroxybenzylidene*, $CHPh_2{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$, *methoxybenzylidene*, $CHPh_2{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe$, and *cinnamylidene*,

$CHPh_2{\cdot}N{\cdot}CH{:}CHPh$, compounds, melting at 131°, 110—111°, and 128°, were prepared from salicylic, anisic, and cinnamic aldehydes; the last named yields a *dibromide* which decomposes at 170—180°; *phenylbenzhydrylaminethiocarbamide*, $CHPH_2{\cdot}NH{\cdot}CS{\cdot}NHPh$, melts at 180·5°. C. F. B.

Derivatives of Unsymmetrical Allylphenylhydrazine and Allyltolylhydrazine. By A. Michaelis and K. Luxembourg (*Ber.*, **26**, 2174—2181).—It was left doubtful whether the compound obtained by the action of mercuric oxide on unsymmetrical allylphenylhydrazine (Abstr., 1889, 1161) is an azo-compound, $NPh{:}NC_3H_5$, or a pyrazole derivative. The former hypothesis is the more probable, for the corresponding cinnamyl compound yields aniline when reduced with zinc and acetic acid; when reduced with sodium amalgam in alcoholic solution, it yields a base, the formula for the oxalate of which is given as $C_6H_5NC_9H_9NH_2,C_2H_2O_4$

$$[?\ NHPh{\cdot}NH{\cdot}C_9H_9,C_2H_2O_4].$$

Thionylallylphenylhydrazone, $C_3H_5{\cdot}NPh{\cdot}N{:}SO$, obtained by shaking an acetic acid solution of allylphenylhydrazine with thionylaniline, is a pale yellow oil decomposed by alkalis. When allylphenylhydrazine, $C_3H_5{\cdot}NPh{\cdot}NH_2$, is treated with pyruvic acid, the *hydrazone*, $C_3H_5{\cdot}NPh{\cdot}N{:}CMe{\cdot}COOH$, separates as a reddish oil, which is converted into *allylindolecarboxylic acid*, $C_6H_4<\begin{matrix}N(C_3H_5)\\CH\end{matrix}>C{\cdot}COOH$, when heated with hydrochloric acid on the water bath. This acid forms white needles which melt at 182° (after sublimation, at 177°); the *barium salt*, with $2H_2O$, crystallises in reddish plates. When heated at 200°, best in a sealed tube, it loses carbonic anhydride, and yields *allylindole*, a colourless liquid which boils at 252°, and will absorb bromine.

Allylphenylhydrazine condenses with ethylic acetoacetate in the presence of zinc chloride to form *ethylic allylmethylindolecarboxylate*, $C_6H_4<\begin{matrix}N(C_3H_5)\\C(COOEt)\end{matrix}>CMe$; it crystallises in small plates. The yield is poor. The *acid* itself forms white needles, and melts at 167—168°; when heated to 180° it evolves carbonic anhydride, and yields *allylmethylindole*, a pale yellow oil of high-boiling point.

Allylparatolylhydrazine, $C_6H_4Me{\cdot}N(C_3H_5){\cdot}NH_2$, was prepared from paratolylhydrazine and allylic bromide; it is a pale yellow oil, which boils at 160—170° under 90 mm. pressure, and rapidly darkens when exposed to the air; the *hydrochloride*, with HCl, forms white plates which melt at 129°, and very quickly redden in the air. With benzoic and cinnamic aldehydes, the hydrazine yields respectively *benzylidene-* and *cinnamylidene-allylparatolylhydrazine*,

$$C_6H_4Me{\cdot}N(C_3H_5){\cdot}N{:}CHPh,$$

&c., the former as white needles melting at 61°, the latter as yellow needles melting at 118°. By ferric chloride, it is oxidised to *diallyldiparatolyltetrazone*, $N_2[N(C_3H_5){\cdot}C_6H_4Me]_2$, which crystallises in plates and melts at 104°; by mercuric oxide, it is oxidised to *azoallyltolyl*,

$C_6H_4Me\cdot N:N\cdot C_3H_5$, which is a white, crystalline substance melting at 96—97°, and distilling at 110° under 20—30 mm. pressure.

C. F. B.

Action of Chlorides of Bibasic acids on Hydrazines. By A. MICHAELIS (*Ber.*, **26**, 2181—2182; compare this vol., i, 370).—Phenylhydrazine hydrochloride, suspended in benzene, and treated with pyrotartaric chloride, yields *phenylmethylorthopiperazone*,

$$\begin{matrix} CHMe\cdot CO\cdot NPh \\ | \quad\quad | \\ CH_2—CO\cdot NH \end{matrix},$$

melting at 204°, the *acetyl derivative* of which melts at 174°; with phthalic chloride, it yields *β*-phthalylphenylhydrazine. With dibromosuccinic chloride, paratolylhydrazine yields a compound $\begin{matrix} CH\cdot CO\cdot N\cdot C_6H_4Me \\ || \quad\quad | \\ CH\cdot CO\cdot NH \end{matrix}$; with succinic chloride itself, *tolylorthopiperazone* $\begin{matrix} CH_2\cdot CO\cdot N\cdot C_6H_4Me \\ | \quad\quad | \\ CH_2\cdot CO\cdot NH \end{matrix}$, is formed. Fumaric chloride does not react with these hydrazines. With acetylphenylhydrazine, succinic chloride yields *acetyl-α-succinylphenylhydrazine*, $C_2H_4(CO\cdot NPh\cdot NHAc)_2$; a similar compound was obtained from acetyltolylhydrazine, and also from fumarylphenyl- and fumaryltolyl-hydrazine. C. F. B.

Bromination of Aromatic Hydrazines and Amines. By L. MICHAELIS (*Ber.*, **26**, 2190—2197).—When bromine is allowed to act on aromatic amines and hydrazines in the presence of strong hydrochloric acid, it enters the benzene ring, preferably in the para-position to the nitrogen atom. In the case of the hydrazines, it also acts as an oxidising agent, converting the brominated derivatives into diazo-compounds; for example, phenylhydrazine yields bromodiazobenzene, in addition to bromophenylhydrazine; and this reaction becomes the chief one, if the above-mentioned para-position is already occupied. The bromination is carried out at 0°, and in the presence of a large excess of concentrated hydrochloric acid. The melting points given are mostly uncorrected.

Phenylhydrazine yields parabromophenylhydrazine, the *acetyl derivative* of which forms colourless prisms melting at 167°, and parabromodiazobenzene. Acetylphenylhydrazine yields acetyldibromophenylhydrazine [$N_2H_2Ac : Br_2 = 1 : 2 : 4$], together with dibromophenylhydrazine and dibromodiazobenzene. Orthotolylhydrazine yields *parabromorthotolylhydrazine* [$Me : N_2H_3 : Br = 1 : 2 : 5$], forming prisms melting at 104°; the *hydrochloride* melts at 183·5°, the *acetate* at 172° with decomposition. It also yields bromorthodiazotoluene, the *perbromide* of which, $C_6H_3MeBr\cdot N_2Br_3$, forms yellowish-red needles, and is converted by ammonia into the *diazoimide*, $C_6H_3MeBr\cdot N_3$, which was obtained crystallised. Paratolylhydrazine yields some *bromoparatolylhydrazine*, crystallising in needles melting at 94·5—95°, together with much *bromoparadiazotoluene*, the *perbromide* of which is an explosive substance and yields a *diazoimide*, which was obtained crystallised. *β*-Naphthylhydrazine yields nothing but *bromodiazonaphthalene*, the *perbromide* of which is an explosive, yellow, crystalline

substance, and yields a *diazoimide*, forming colourless needles, and melting at 111°. α-Naphthylamine yields *bromo-α-naphthylamine*, which crystallises in small, white needles, and melts at 118·5°; the *hydrochloride* forms white prisms, which decompose above 200°. β-Naphthylamine yields dibromo-β-naphthylamine [$NH_2 : Br_2 = 2 : 1 : 3$]. C. F. B.

Benzylbenzaldoxime. By E. Beckmann (*Ber.*, **26**, 2272—2285; Abstr., 1891, 194).—Benzylbenzaldoxime, $O<\overset{CHPh}{N\cdot C_7H_7}$, when dissolved in benzene and treated with benzoic chloride, gives a precipitate of benzylbenzaldoxime hydrochloride which, after a time, dissolves, and the mixture then deposits benzylbenzamide, $NH\cdot Bz\cdot C_7H_7$. 0·045 gram of benzoic chloride is sufficient to convert 1 gram of the benzaldoxime into benzylbenzamide. In ethereal solution, a small quantity of benzylbenzamide is obtained, and then a separation of beautiful lustrous needles takes place, which contain benzylbenzamide and benzylbenzaldoxime in molecular proportion. If benzylbenzaldoxime is treated with benzoic chloride at low temperatures without any solvent, benzylbenzamine is obtained, and at the boiling temperature a mixture of benzylbenzamide and benzoylbenzylbenzamide. Benzoic anhydride has no action on benzylbenzaldoxime at low temperatures; at 120—180°, however, benzoylbenzylbenzamide is formed.

Benzoylbenzylbenzamide, $NBz_2\cdot C_7H_7$, melts at 107—108°; when heated at higher temperature, it yields a deep blue liquid which gives a blue solution in alcohol, turns green when treated with acids, and is decolorised by reducing agents. It is not altered by aqueous potassium hydroxide, boiling acetic acid, or acetic anhydride, and when boiled with benzoic anhydride is converted into benzoylbenzamide.

Acetic chloride and acetic anhydride act on benzylbenzaldoxime in a similar way to benzoic chloride and anhydride respectively. *Acetylbenzylbenzamide*, $NAcBz\cdot C_7H_7$, was obtained as an oil which was not pure. When heated at high temperatures, it yields a blue compound, and when treated with sodium and alcohol is converted into benzylbenzamide.

Phosphoric chloride and phosphorus anhydride, used in relatively small quantities, convert benzylbenzaldoxime into benzylbenzamide, in a similar way to the above acid chlorides. A mixture of acetic acid, acetic anhydride, and hydrogen chloride behaves similarly. Hydrochloric acid, acetic acid, and alcohol are without action on benzylbenzaldoxime.

α-Benzoyl-β-benzylhydroxylamine, $C_7H_7\cdot NH\cdot O\cdot COPh$, is obtained by shaking the aldoxime with ether and benzoic chloride, and after separating the precipitate of benzylbenzaldoxime hydrochloride, allowing the solution to evaporate by exposure to air. The product it then treated with soda, when the hydroxylamine derivative is obtained as an oil; if treated with sodium and alcohol, it yields ethylic benzoate and benzoic acid. When subjected to steam distillation in the presence of alkali, or when heated with hydrochloric acid, β-benzoylhydroxylamine is obtained. The *benzoyl derivative*, $C_7H_7\cdot NBz\cdot O\cdot COPh$, is obtained by boiling it with benzoic chloride.

It crystallises in tablets, melts at 96—97°, and, when treated with sodium and alcohol, yields ethylic benzoate and β-benzoyl-β-benzylhydroxylamine; the latter crystallises in white needles and melts at 106°.

α-Acetyl-β-benzylhydroxylamine, $C_7H_7{\cdot}NH{\cdot}OAc$, is obtained in a similar way to the preceding compound; it is an oil. The *hydrochloride* melts at 105—110°. When boiled with acetic chloride, the oily *diacetyl compound*, $C_7H_7{\cdot}NAc{\cdot}OAc$, is obtained; the latter, when treated with sodium and alcohol, yields the compound $C_7H_7NAc{\cdot}OH$, which crystallises in tablets, and melts at 124°.

E. C. R.

Action of Isocyanates on Aromatic Aldoximes. By H. Goldschmidt and W. H. van Rietschoten (*Ber.*, **26**, 2087—2100).—Carbanilidoparamethoxybenzosynaldoxime (m. p. 80°) has previously been described (Abstr., 1890, 1261); on recrystallisation from warm ether, an isomeric compound is formed in aggregates of colourless needles; this melts at 82° with evolution of gas, and on treatment with soda yields methoxybenzonitrile, together with very small quantities of diphenylcarbamide and regenerated aldoxime. Carbanilidoparamethoxybenzantialdoxime could only be obtained in one modification melting at 103°, instead of 82° as previously stated. *Carborthotoluidoparamethoxybenzosynaldoxime*, $\begin{matrix}OMe{\cdot}C_6H_4{\cdot}CH\\ \|\\ N{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me\end{matrix}$, is formed from orthotolylic isocyanate and the synaldoxime, at ordinary temperatures, and crystallises in greenish, flat prisms melting at 81° with decomposition. On warming with ether, a second modification is obtained in colourless, dendritic needles melting at 98°. *Carborthotoluidoparamethoxybenzantialdoxime*, $\begin{matrix}OMe{\cdot}C_6H_4{\cdot}CH\\ \|\\ C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}NO\end{matrix}$, only exists in one form, crystallising in clusters of colourless needles which melt at 127°. *Carboparatoluidoparamethoxybenzosynaldoxime* is prepared by the action of paratolylic isocyanate on either the "syn-" or "anti-" aldoxime, and is deposited in pale yellow prisms which become colourless on heating to 70—80°, and melt at 106° with evolution of gas. On treatment with soda, it is resolved into paraditolylcarbamide, paratoluidine, paramethoxybenzonitrile, and, in relatively large quantity, regenerated synaldoxime. The isomeric compound is formed by boiling with ether, and crystallises in long, slender needles melting at 106° with decomposition. By the action of soda, it yields the same products as the yellow substance; the amount of aldoxime is, however, small, that of nitrile large. *Carboparatoluidoparamethoxybenzantialdoxime* is obtained from the mother liquor after the removal of the yellow "syn-" derivative, but the most favourable conditions for its formation from the antialdoxime have not yet been determined. It is deposited from benzene in colourless crystals melting at 126°. An isomeric derivative could not be obtained.

Orthomethoxybenzantialdoxime is not altered by the successive action of hydrogen chloride and soda. The following carbanilido- and carbotoluido-derivatives were prepared by the action of phenylic isocyanate and of the tolylic isocyanates on the "syn-" and "anti-"

aldoximes in ethereal solution at ordinary temperatures; the isomeric modifications were obtained by heating the additive compounds with ether. Carbanilidorthomethoxybenzantialdoxime, $\begin{matrix}OMe\cdot C_6H_4\cdot CH\\ \|\\ NHPh\cdot CO\cdot O\cdot N\end{matrix}$, has been previously described, and exists only in one modification. *Carborthotoluidorthomethoxybenzantialdoxime*, $\begin{matrix}OMe\cdot C_6H_4\cdot CH\\ \|\\ C_6H_4Me\cdot NH\cdot CO\cdot O\cdot N\end{matrix}$, crystallises in colourless prisms, and melts at 106°. On hydrolysis with soda, the oxime is regenerated. In addition to the above crystals, an oily liquid is formed in small quantity; this may be an isomeric modification, as on treatment with soda it yields orthoditolylcarbamide, orthotoluidine, and the original oxime. *Carboparatoluidorthomethoxybenzantialdoxime* crystallises in colourless, transparent needles melting at 131°; a second modification could not be obtained.

The additive compounds of cuminantialdoxime appear only to exist in one modification, and do not yield derivatives of the synaldoxime. *Carbanilidocuminantialdoxime*, $\begin{matrix}C_6H_4Pr^{\beta}\cdot CH\\ \|\\ NHPh\cdot CO\cdot O\cdot N\end{matrix}$, crystallises in thick, colourless prisms melting at 89°. *Carborthotoluidocuminantialdoxime*, $\begin{matrix}C_6H_4Pr^{\beta}\cdot CH\\ \|\\ C_6H_4Me\cdot NH\cdot CO\cdot O\cdot N\end{matrix}$, is deposited in small needles, and melts at 70°.

Carboparatoluidocuminantialdoxime crystallises in colourless plates melting at 115°. *Carboparatoluidocuminosynaldoxime*,

$$\begin{matrix}C_6H_4Pr^{\beta}\cdot CH\\ \|\\ N\cdot O\cdot CO\cdot NH\cdot C_6H_4Me'\end{matrix}$$

is deposited in pale yellow needles; it becomes colourless at 70—75°, and melts at 113° with decomposition. The isomeric modification crystallises in colourless needles, and melts at 120°.

Paranitrobenzantialdoxime gives neither isomeric additive products with isocyanates, nor derivatives of the synaldoxime. *Carborthotoluidoparanitrobenzantialdoxime*, $\begin{matrix}NO_2\cdot C_6H_4\cdot CH\\ \|\\ C_6H_4Me\cdot NH\cdot CO\cdot O\cdot N\end{matrix}$, crystallises in yellow needles melting at about 183°. *Carboparatoluidoparanitrobenzantialdoxime* forms slender, yellowish needles, and melts at 154°. *Carborthotoluidoparanitrobenzosynaldoxime*,

$$\begin{matrix}NO_2\cdot C_6H_4\cdot CH\\ \|\\ N\cdot O\cdot CO\cdot NH\cdot C_6H_4Me'\end{matrix}$$

is deposited in yellow, rhombic plates; it begins to decompose at 100°, and melts at about 185°. *Carboparatoluidoparanitrobenzosynaldoxime* crystallises in transparent, pale yellow plates; it softens under 100° and melts at about 176° with decomposition.

Metanitrobenzantialdoxime gives isomeric additive products with isocyanates, but does not yield "syn-" derivatives. Carbanilidometanitrobenzantialdoxime (m. p. 105°) has been previously described by Goldschmidt and Ernst (Abstr., 1890, 1261); on treatment with soda,

it yields diphenylcarbamide, aniline, and the oxime; by the action of ether at ordinary temperatures, it is slowly converted into an isomeric modification; the change occurs more rapidly in presence of hydrogen chloride, or on boiling with alcohol or benzene. The compound crystallises in small, yellow needles, melts at 139° with decomposition, and, on hydrolysis, yields the same substances as its isomeride. *Carboparatoluidometanitrobenzantialdoxime* forms small, yellow, transparent needles melting at about 185°, with previous softening at about 96°. The second modification, prepared in a similar manner to the corresponding carbanilido-derivative, crystallises in yellow, transparent prisms, and melts at 132°. Both compounds, on hydrolysis, yield paratoluidine, paraditolylcarbamide, and regenerated oxime. *Carborthotoluidometanitrobenzantialdoxime* appears to exist in one form only; it forms yellow crystals, which melt at 138° with evolution of gas and previous softening. *Carboparatoluidometanitrobenzosynaldoxime* crystallises in yellow, microscopic needles; it begins to decompose at 100—103°, and melts at 185°. The authors are unable to explain the occurrence of two isomeric carbanilidometanitrobenzantialdoximes (see above); it is possible that the nitrogen atom of the NH group is asymmetric, although both compounds are optically inactive; on chemical grounds, there appears to be no evidence to show that the substances are represented by different structural formulæ, such as $HO\cdot\overset{\|}{C}\cdot O\cdot\overset{\|}{N}$ and $HO\cdot\overset{\|}{C}\cdot O\cdot\overset{\|}{N}$, or

$NO_2\cdot C_6H_4\cdot\overset{\|}{C}H$ and $NO_2\cdot C_6H_4\cdot\overset{\|}{C}H$

NPh PhN

$NO_2\cdot C_6H_4\cdot CH{:}N\cdot O\cdot CO\cdot NHPh$ and $NO_2\cdot C_6H_4\cdot CH{:}NO\cdot C(OH){:}NPh$.

The above results prove that paramethoxybenzantialdoxime differs from benzantialdoxime, but resembles the corresponding thiophen- and furfur-aldoximes in yielding "syn-" additive compounds with the tolylic isocyanates. Further, that the formation of isomeric carbanilido-derivatives, which was first observed by Beckmann in the case of carbanilidobenzosynaldoxime (Abstr., 1891, 193), occurs with tolerable frequency. J. B. T.

Isomeric Orthonitrobenzaldoximes. By H. Goldschmidt and W. H. van Rietschoten (*Ber.*, **26**, 2100—2103).—It has been shown that many ortho-substituted benzantialdoximes are not converted into the isomeric synaldoximes by Beckmann's method; to this rule orthonitrobenzaldoxime is an exception. *Carbanilidorthonitrobenzantialdoxime*, $NO_2\cdot C_6H_4\cdot\overset{\|}{C}H$ / $NHPh\cdot CO\cdot O\cdot\overset{\|}{N}$, forms colourless crystals melting at about 88°. *Carboparatoluidorthonitrobenzantialdoxime*, $NO_2\cdot C_6H_4\cdot\overset{\|}{C}H$ / $C_6H_4Me\cdot NH\cdot CO\cdot O\cdot\overset{\|}{N}$, is prepared either from the pure oxime, or by heating a mixture of the "anti-" and "syn-" oximes with paratolylic isocyanate in benzene solution; it crystallises in small, colourless needles, melts at 139°, and on treatment with soda yields orthonitrobenzantialdoxime, paratoluidine, and in small quantity paraditolylcarbamide. *Orthonitro-*

benzosynaldoxime, $NO_2 \cdot C_6H_4 \cdot C\overset{\|}{H}$ (N·OH), is obtained by treatment of the antialdoxime with hydrogen chloride in ethereal solution; the resulting salt, which melts at 87°, is decomposed with soda, and the product crystallised from benzene. It melts at 136°, and is somewhat more sparingly soluble than the antialdoxime, into which it is readily converted. The *carbanilido-derivative*, $NO_2 \cdot C_6H_4 \cdot C\overset{\|}{H}$ (N·O·CO·NHPh), is deposited in yellow prisms melting at 91°, with evolution of gas. The *carboparatoluidide*, $NO_2 \cdot C_6H_4 \cdot C\overset{\|}{H}$ (N·O·CO·NH·C_6H_4Me), resembles the preceding compound, and melts at 93° with decomposition. *Orthonitrobenzaldoxime methyl ether*, $NO_2 \cdot C_6H_4 \cdot CH<\overset{NMe}{O}$, is prepared by the action of sodium methoxide and methylic iodide on the synaldoxime in methyl alcoholic solution at ordinary temperatures, and is deposited from ether in long, yellow crystals melting at 92°. The constitution of the compound is proved by its resolution into orthonitrobenzaldehyde and methylhydroxylamine when heated with dilute sulphuric acid. By the action of hydriodic acid at 100° under pressure, methylamine is formed.

Orthonitrobenzosynaldoxime methyl ether $NO_2 \cdot C_6H_4 \cdot C\overset{\|}{H}$ (N·OMe), is obtained by treating the silver salt of the oxime with methylic iodide in ethereal solution; it is a colourless, slightly viscid liquid, and is readily converted into the "anti-" ether (m. p. 58°) by the action of hydrogen chloride. J. B. T.

Hydrocinnamaldoxime: A Correction. By W. Dollfus (*Ber.*, **26**, 1970—1972).—In a former paper (Abstr., 1892, 1174) the author described the preparation of hydrocinnamaldehyde from chromyl chloride and propylbenzene, quite overlooking v. Miller's observation (Abstr., 1190, 978) that the product of this reaction is methyl benzyl ketone. He now describes the following derivatives of hydrocinnamaldehyde, a sample of this compound, prepared by distilling calcium hydrocinnamate with calcium formate, having been furnished him by v. Miller.

Hydrocinnamaldoxime, $CH_2Ph \cdot CH_2 \cdot CH{:}NOH$, crystallises from alcohol in long prisms, and melts at 93—94·5°; it yields hydrocinnamonitrile when treated with acetic anhydride or acetic chloride. The substance previously prepared from methyl benzyl ketone (*loc. cit.*), and described as hydrocinnamonitrile, is now found to be a mixture. A. R. L.

Stereoisomerism of the Benzhydroxamic acids. By A. Hantzsch and A. Werner (*Ber.*, **26**, 2069—2070).—A reply to Lossen (this vol., i, 572).

Action of Hydrazine on Imido-ethers. By A. Pinner (*Ber.*, **26**, 2126—2135).—By the action of hydrazine (3 mols.) on benzimide ethyl ether (2 mols.) in dilute alcoholic solution at ordinary

temperatures, numerous products are formed, of which six have been isolated in the manner described by the author, taking advantage of differences in their basicities and solubilities.

Dibenzenylhydrazidine, $C_{14}H_{14}N_4$, crystallises from chloroform in yellowish, lustrous plates melting at 202°, without decomposition. It is not acted on by oxidising agents at ordinary temperatures, and probably, therefore, has the formula $N_2(CPh{\cdot}NH_2)_2$, rather than $N_2H_2(CPh{:}NH)_2$. The *hydrochloride* crystallises in lustrous needles; the *platinochloride* in yellow prisms. On treatment with nitrous acid, the hydrazidine is converted into dibenzoylhydrazine. This hydrazidine is accompanied by a second basic compound, $C_{21}H_{21}N_5O$, which occurs in small quantity, is almost insoluble in chloroform, and crystallises in silky, lustrous needles melting at 170°. Its investigation is incomplete. The *hydrochloride* is readily soluble; the *platinochloride* is amorphous.

Benzenylimidonitrile, $CPh\begin{cases}NH\\|\\N\end{cases}$, is probably formed by elimination of ammonia from the intermediate compound, $NH{:}CPh{\cdot}NH{\cdot}NH_2$; it is readily soluble in dilute alcohol, crystallises in colourless plates, begins to soften at about 240°, and melts at 258°. The *hydrochloride* and *platinochloride* are crystalline.

Diphenyldihydrotetrazine, $CPh\begin{cases}N\text{——}N\\NH{\cdot}NH\end{cases}CPh$, is the chief product of the reaction, and crystallises in long, colourless, slender needles; the compound exhibits feebly basic properties, and is converted into the corresponding tetrazine (see below) by heating, or by the action of air or oxidising agents. The *diacetyl derivative*,

$$CPh\begin{cases}N\text{——}N\\NAc{\cdot}NAc\end{cases}NPh,$$

forms colourless, crystalline plates, and melts at 228—229°.

Diphenyltetrazine, $CPh\begin{cases}N{\cdot}N\\N{:}N\end{cases}CPh$, is readily prepared from the preceding compound by oxidation; it forms flat, bluish-red prisms, and melts at 192°. It is soluble in concentrated sulphuric acid with a red coloration, and is precipitated on dilution; it is not acted on by a mixture of sulphuric acid and fuming nitric acid at ordinary temperatures. By treatment with reducing agents the dihydrogen derivative is regenerated.

A compound, $C_{14}H_{12}N_2$, which it is proposed to term *dibenzimidine*, $NH(CPh{:}NH)_2$ (compare Abstr., 1892, 1110), has also been obtained. After treatment with water, it crystallises from ethylic acetate with $2H_2O$ in prisms melting at 80°; the anhydrous substance melts at 131°. It is suggested that this compound is formed from dibenzenylhydrazidine by the action of alkali in a manner similar to that in which the osotetrazones are converted into the osotriazones. The action of hydrazine on acetimidoethyl ether is under investigation; the products are extremely volatile and difficult to isolate.

J. B. T.

Constitution of Hydrocyanorosaniline and of Magenta. By E. Fischer and W. L. Jennings (*Ber.*, **26**, 2221—2225).—E. and O.

Fischer (*Annalen*, **194**, 275) looked on hydrocyanopararosaniline as the triamido-derivative of a cyanotriphenylmethane, but were unable to prepare the latter by the aid of the diazo-reaction. When, however, the base is diazotised, and then treated by the Sandmeyer-Gattermann method, triphenylacetonitrile, $CPh_3{\cdot}CN$ is readily obtained. It melts at 127°, and is identical in its properties with the substance prepared from triphenylmethylic bromide and mercuric cyanide. Hydrocyanopararosaniline has therefore the constitution

$$(NH_2{\cdot}C_6H_4)_3C{\cdot}CN.$$

Rosenstiehl (Abstr., 1893, i, 332) has proposed for the salts of pararosaniline the formula $(NH_2{\cdot}C_6H_4)_3C{\cdot}X$, so that in view of the close analogy of similarly constituted chlorine and cyano-derivatives, the pararosaniline salts should be very similar to hydrocyanopararosaniline. The opposite of this is, however, the case, and the Rosenstiehl formulæ, moreover, do not exhibit the relations of pararosaniline to aurine, and of magenta to rosolic acid. On the other hand the formulæ proposed by Nietzki (*Chemie der organischen Farbstoffe*, 1889, 88),

$$(NH_2{\cdot}C_6H_4)_2{:}C_6H_4{:}NH,HCl \quad \text{and} \quad (HO{\cdot}C_6H_4)_2{:}C_6H_4{:}O,$$
Paramagenta. Aurin.

agree with all the observed facts, and, in fact, are simply related to the older formulæ, $C_6H_4{<}\begin{matrix}C(C_6H_4{\cdot}NH_2)_2\\ |\\ NH,HCl\end{matrix}$ and $C_6H_4{<}\begin{matrix}C(C_6H_4{\cdot}OH)_2\\ |\\ O\end{matrix}$, in the same way as the diketone formula, $O{:}C_6H_4{:}O$ for quinone, is to the peroxide formula, $C_6H_4{<}\begin{matrix}O\\ |\\ O\end{matrix}$.

The chemical analogy of the rosaniline compounds to the quinones is very striking, and was pointed out long ago by Graebe and Caro (*Annalen*, **179**, 184); the combination of the rosaniline salts with three additional molecules of acid, which led Rosenstiehl to propose his new formula, is quite analogous to the combination of quinone with hydrochloric acid. The constitution of the rosaniline salts containing 4 mols. of acid cannot, however, be considered as yet settled.

The application of the Sandmeyer-Gattermann method to the diazo-compound of pararosaniline has led to the conversion of this substance into triphenylcarbinol, and thus confirmed the view taken by E. and O. Fischer, who were unable at the time of their research to accomplish this transformation. A. H.

Action of Amides on Benzaldehyde. By K. Bülow (*Ber.*, **26**, 1972—1974).—*Benzylidenediformamide*, $CHPh(NH{\cdot}CHO)_2$, is obtained by heating benzaldehyde and formamide together on the water bath for 24 hours; it crystallises from water in white, silky needles, melts at 149—150°, is insoluble in ether, and reduces alkaline silver solutions. If heated with water in a sealed tube at 100°, or treated with 0·1 per cent. hydrochloric acid at the ordinary temperature, it is hydrolysed into its components. When benzaldehyde

is boiled with formamide in a reflux apparatus for two hours, tetraphenylpyrazine (m. p. 246—247°), together with other compounds, is obtained. Roth's benzylidenediacetamide (*Annalen*, **154**, 72) is formed by heating benzaldehyde with acetamide on the water bath; 100 parts of water dissolve 3 parts at 100°, and 1 part at 20°. When benzaldehyde is boiled for 5—7 hours with acetamide, tetraphenylpyrazine and other compounds are obtained. Benzylidenedibenzamide (Roth, *loc. cit.*) is formed, together with other compounds and a small quantity of tetraphenylpyrazine, when benzaldehyde is boiled with benzamide.

A. R. L.

Iodoso-compounds, a Reply to C. Willgerodt. By V. Meyer (*Ber.*, **26**, 2118—2122).—A polemical paper criticising generally Willgerodt's work on iodoso-compounds, and referring particularly to his last communication on the subject (this vol., i, 503). Iodosobenzoic acid is very different in appearance and properties from iodoxybenzoic acid; the former crystallises in light, silvery, lustrous plates, melts without detonation, has no sour taste, and is more phenolic than acidic in properties. Iodoxybenzoic acid forms dense, granular crystals, has a strongly-marked acid reaction and taste, and explodes on heating. The specimen of iodosobenzoic acid which undergoes decomposition at 244° is, contrary to Willgerodt's suggestion, the purest form of the acid hitherto prepared, and it is not altered by crystallisation from glacial acetic acid. The author has prepared a toxic base containing iodine, but free from nitrogen, from iodosobenzene, and from iodoxybenzene; its salts resemble those of thallium; the sulphate is soluble; the haloïd salts are insoluble. The base, which is liberated by the action of moist silver oxide on the salts, is soluble in water, and has a strongly alkaline reaction. It is being further investigated.

J. B. T.

Hydrogenised Paratoluic acids. By A. Einhorn and R. Willstätter (*Ber.*, **26**, 2009—2010).—When paramethylenehydrobenzoic acid (this vol., i, 378) is reduced at the ordinary temperature, it is converted into *tetrahydroparatoluic acid*. The latter solidifies to colourless needles when cooled in a freezing mixture, but is liquid at the ordinary temperature; it boils at 250—253°, has a characteristic pungent odour, and instantly decolorises a solution of permanganate. The *calcium* salt crystallises in white needles with $4H_2O$; the *copper* salt forms deep blue aggregates of thin tablets with $2H_2O$; the *methylic* salt boils at 210—220°; and the *amide* melts at 157—158°. *Paramethylenehydrobenzamide* melts at 125·5°.

When tetrahydroparatoluic acid is boiled with a solution of sodium hydroxide, it is converted into an *isomeride;* this boils at 254—260°, and solidifies readily. It crystallises from alcohol in colourless leaflets, is devoid of odour, and melts at 45—47°. The *calcium* salt, with $4H_2O$, differs in solubility from that of the isomeride; the *methylic* salt resembles the isomeric compound; and the *amide* melts at 134—135°.

A. R. L.

Hexahydroisophthalic acid. By V. Villiger (*Annalen*, **276**, 255—265).—Isophthalic acid is prepared by treating boiling meta-

xylene with dry bromine (2 mols.), digesting the crystalline product on the water bath with an excess of alcoholic potassium acetate, and heating the diacetate thus obtained on the water bath with an alkaline solution of potassium permanganate. The dry barium salt prepared from the crude acid is extracted with cold water, which dissolves the barium metatoluate. The yield of pure isophthalic acid is 100 per cent. of the metaxylene.

To reduce isophthalic acid, it is dissolved in a solution of sodium carbonate (70 grams) in water (300 c.c.), and treated in presence of a current of carbonic anhydride with about 2 kilos. of a 3 per cent. sodium amalgam at 40—50°, the amalgam being added in the course of two days, in portions of 50 grams at a time. The crude product is heated at 100° in a sealed tube with concentrated hydrobromic acid for 20 hours, and the hydrobromide treated with zinc dust and acetic acid, or preferably with sodium amalgam in presence of carbonic anhydride. A mixture of the two hexahydroisophthalic acids, synthesised by W. H. Perkin, jun. (Trans., 1891, 798), is obtained; they can be separated by following his directions, and agree in every particular with his description.

The paper concludes with some remarks by v. Baeyer, who draws attention to the fact that the hexahydro-derivatives of all three benzenecarboxylic acids resemble the aliphatic acids containing the same number of carbon atoms between the carboxyl groups (see also Perkin, *loc. cit.*). A. R. L.

Action of Benzaldehyde on Ethylic Oxalacetate. By W. Wislicenus (*Ber.*, **26**, 2144—2147).—The product of this reaction is not ethylic hydrogen benzylideneoxalacetate, as previously supposed (this vol., i, 146), for it does not take up bromine, nor yield an ethylic salt; it is doubtless *ethylic ketophenylparaconate*,

$$O<\begin{matrix}CO\cdot CO\\ CHPh\end{matrix}>CH\cdot COOEt.$$

Its *sodium derivative*, $C_{13}H_{11}O_5Na$, is a white crystalline substance, and, when reduced with sodium amalgam, it yields *ethylic phenylhydroxyparaconate*, $O<\begin{matrix}CO\cdot CH(OH)\\ CHPh\end{matrix}>CH\cdot COOEt$, which crystallises in small, white needles, melting at 86—88°.

The last substance, when boiled with caustic soda, yields the sodium salt of *phenylhydroxyitamalic acid*,

$$OH\cdot CHPh\cdot CH(COOH)\cdot CH(OH)\cdot COOH,$$

the *silver salt* of which, $C_{11}H_{10}O_6Ag_2$, is a white powder.

C. F. B.

Action of Formaldehyde on Benzenesulphonamide. By A. Magnus-Levy (*Ber.*, **26**, 2148—2150).—When an alcoholic solution of benzenesulphonamide is heated with a 40 per cent. aqueous solution of formaldehyde and a little hydrochloric acid, *tribenzenesulphonetrimethylenetriimide*, $C_3H_6N_3(SO_2Ph)_3$, is formed, together with the analogous dimolecular compound $C_2H_4N_2(SO_2Ph)_2$. The former crystallises in white needles, melts at 217°, and is nearly insoluble in

hot alcohol; the latter forms lustrous needles, melts at 132°, and dissolves readily in alcohol. These compounds contain respectively a 6- and a 4-membered ring, consisting of alternate carbon and nitrogen atoms. C. F. B.

Action of Phosphorus Pentachloride on Orthobenzoicsulphinide. By J. A. Jesurin (*Ber.*, **26**, 2286—2298).—The compound described by Brackett (Abstr., 1888, 282), obtained by the successive action of phosphorus pentachloride and methyl alcohol on orthobenzoicsulphinide, is shown by the author to be *methylic orthosulphaminebenzoate*, $COOMe\cdot C_6H_4\cdot SO_2NH_2$. It is prepared by heating orthobenzoicsulphinide for two hours at the ordinary pressure at 70—75° with phosphorus pentachloride, and pouring the product into well-cooled methyl alcohol; or by passing hydrogen chloride into a solution of orthobenzoicsulphinide in methyl alcohol. It melts at 125—126°, and, like the corresponding ethylic compound (Abstr., 1881, 816; 1888, 367), yields salts of orthobenzoicsulphinide when boiled with alkalis and ammonia.

When orthobenzoicsulphinide is heated with phosphorus pentachloride at 70—75° in a sealed tube, *orthocyanobenzenesulphonic chloride*, $CN\cdot C_6H_4\cdot SO_2Cl$, is obtained; it separates from benzene in stout crystals, melts at 69—70°, and yields *orthocyanobenzenesulphonic acid* when boiled with water; this acid could not be isolated, but the *sodium salt*, $CN\cdot C_6H_4\cdot SO_3Na + H_2O$, crystallises in prisms. If orthocyanobenzenesulphonic chloride is heated in a sealed tube at 95—100° with a little water, the eliminated hydrogen chloride converts the orthocyanobenzenesulphonic acid initially formed into orthobenzaminesulphonic acid (Abstr., 1889, 709); whilst at 180° the action proceeds further, and *ammonium hydrogen orthosulphobenzoate*,

$$COOH\cdot C_6H_4\cdot SO_3NH_4,$$

is formed, a fact which shows that orthosulphobenzoic acid is a stronger acid than hydrochloric acid; indeed, when concentrated solutions of orthosulphobenzoic acid and ammonium chloride are heated together, ammonium hydrogen orthosulphobenzoate is obtained. When orthocyanobenzenesulphonic chloride is heated with alcohol, orthobenzaminesulphonic acid, ethylic chloride, and ether are formed. The *sulphonamide*, $CN\cdot C_6H_4\cdot SO_2NH_2$, is obtained by treating the chloride with a solution in benzene containing exactly twice the molecular proportion of ammonia; it crystallises in leaflets, melts at 260°, and is almost insoluble in benzene, but fairly soluble in cold water and alcohol. It dissolves in aqueous ammonia, and when the solution is heated, an isomeric *compound*, $C_6H_4<\begin{matrix}C(NH_2)\\SO_2\end{matrix}>N$, separates (see below); the third isomeride (diimide) is probably also formed, but it appears to decompose when boiled with water into orthobenzoicsulphinide. The *anilide*, $CN\cdot C_6H_4\cdot SO_2\cdot NHPh$, is obtained by treating orthocyanobenzenesulphonic chloride with aniline; it melts at 150—152°; whilst by heating the chloride with aniline in a sealed tube at 150°, an *isomeric compound*, $C_6H_4<\begin{matrix}C(NHPh)\\SO_2\end{matrix}>N$, is obtained, insoluble in benzene, and not melting at 315°, together with a com-

pound, $C_6H_4<\overset{C(NPh)}{SO_2}>NPh$, which crystallises from benzene in yellow needles, and melts at 187—189°.

The *chloride*, $C_6H_4<\overset{CCl}{SO_2}>N$, is obtained by heating orthobenzoicsulphinide at 180° under ordinary pressure with phosphorus pentachloride (2 mols.); it crystallises from benzene in small needles, melts at 143—145°, and yields orthobenzoicsulphinide when treated with water. The *ethyl ether*, $C_6H_4<\overset{C(OEt)}{SO_2}>N$, is obtained by boiling the chloride with absolute alcohol; it crystallises in flat needles, melts at 217—218°, and decomposes when heated with water at 150° in a sealed tube into orthobenzoicsulphinide and orthosulphaminebenzoic acid; at 280—300° the product is principally ammonium hydrogen orthosulphobenzoate. The *methyl* ether melts at 182—183°. The *amide*, $C_6H_4<\overset{C(NH_2)}{SO_2}>N$, is prepared by heating the analogous chloride with ammonium carbonate, or by heating it with a solution of ammonia in benzene; it is likewise obtained as above mentioned, and also by treating orthocyanobenzenesulphonic chloride with an excess of ammonia, or the last-described ethyl ether with alcoholic ammonia; it is almost insoluble in cold water, but separates from hot water in small, stout crystals, and does not melt at 300°. When heated with aniline in a sealed tube at 170—180°, it yields the anilide described above.

Orthochlorobenzonitrile, $CN\cdot C_6H_4Cl$ (Henry, *Ber.*, **2**, 492), is obtained by heating orthobenzoicsulphinide with phosphoric chloride at 230°.

The author considers that the following experiments justify the assumption that orthobenzoicsulphinide has the constitution

$$C_6H_3<\overset{CO}{SO_2}>NH;$$

the pseudo-modification, $C_6H_4<\overset{C(OH)}{SO_2}>N$, appears to be incapable of existence, although several of its derivatives have been prepared.

A. R. L.

Action of Phosphorus Pentachloride on Orthobenzoicsulphinide. By C. FAHLBERG (*Ber.*, **26**, 2299).—The experiments described in Jesurin's paper (preceding abstract) were made at the author's suggestion. Now that technical orthobenzoicsulphinide can be readily purified (Eng. Pat. of 1891, No. 22,787), additional facilities are offered for its study. A. R. L.

Synthesis of Indene and Hydrindene. By W. H. PERKIN, Jun., and G. RÉVAY (*Ber.*, **26**, 2251—2254).—Indene is obtained by the distillation of barium hydrindenecarboxylic acid either alone or in presence of sodium methoxide. This synthetic indene has most of the properties of the indene isolated by Krämer and Spilker from coal tar (Abstr., 1891, 205), and gives the same hydrindene on reduction. It differs, however, in sp. gr., refractive index, and magnetic rotation, which may be due to traces of impurities; but the authors

point out that two isomeric indenes are possible, of the formulæ $C_6H_4<\begin{matrix}CH\\CH_2\end{matrix}>CH$ and $C_6H_4<\begin{matrix}CH\\\|\\CH\end{matrix}>CH_2$, which would yield the same hydrindene on reduction. Both products boil at 180°, and give a reddish-brown resin with sulphuric acid.

Methylic hydrindenecarboxylate, $C_9H_9{\cdot}COOMe$, is a colourless oil, boils at 170° under 60 mm. pressure, and, after some time, solidifies in tabular crystals.

Hydrindenecarboxylic chloride, obtained by the action of phosphorus pentachloride on the acid, boils at 180° under 100 mm. pressure, crystallises on cooling in large, colourless crystals, and melts at 38°. The *amide* crystallises in lustrous prisms, and melts at 178°. The *anilide* melts at 182°.

Tetrabromhydrindenecarboxylic acid, $C_9H_5Br_4{\cdot}COOH$, is obtained by the action of bromine vapour on hydrindenecarboxylic acid. It crystallises in needles, and melts at 248—250°.

Indenecarboxylic acid is obtained by the action of bromine on a solution of hydrindenecarboxylic acid in chloroform at 100°. It crystallises from acetic acid in needles, softens at 220°, and melts at 230°.

Hydrindene methyl ketone, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH{\cdot}COMe$, is obtained by the action of zinc methide on an ethereal solution of hydrindenecarboxylic chloride. It boils at 180—185° under 70 mm. pressure. The *oxime* crystallises in large, lustrous prisms, and melts at 127°.

Hydrindenemethylcarbinol, $C_9H_9{\cdot}CHMe{\cdot}OH$, obtained from the ketone by reduction with sodium and alcohol, melts at 45°, and boils at 185—190° under 80 mm. pressure. The *acetate* boils at 188—190° under 70 mm. pressure.

Hydrindene ethyl ketone melts at 28° and boils at 188—190° under 80 mm. pressure. The *oxime* melts at 105°. *Hydrindeneethylcarbinol* boils at 192° under 80 mm. pressure, crystallises from alcohol in beautiful, colourless needles, and melts at 63°. The *acetate* boils at 210° under 80 mm. pressure.

Hydrindene phenyl ketone, obtained by the action of benzene on hydrindenecarboxylic chloride in the presence of aluminium chloride, crystallises in slender needles, and melts at 107°.

Bromine acts very readily on a solution of hydrindene in chloroform with the formation of *dibromhydrindene*, which boils at 180—185° under 50 mm. pressure. If, however, the crude product is distilled at the ordinary pressure, hydrogen bromide and *monobromhydrindene* are obtained. The latter boils at 242—244°, and, when oxidised with nitric acid, yields 1 : 2 : 4-bromophthalic acid melting at 162—164°, and yielding an anhydride which melts at 106°. E. C. R.

Conversion of Carbazole into Indole. By C. U. Zanetti (*Ber.*, **26**, 2006—2008).—Tetrahydrocarbazole is obtained more readily by boiling carbazole with sodium and amyl alcohol than by Graebe and Glaser's method (*Annalen*, **163**, 352). When tetrahydrocarbazole is fused with potash, α-indolecarboxylic acid (Ciamician and Zatti, Abstr., 1888, 957) is produced. A. R. L.

"Hydrocoton" and its Derivatives. By O. Hesse (*Annalen*, **276**, 328—342; compare Ciamician and Silber, Abstr., 1892, 62, and 873; this vol., i, 409 and 417).—*Bromhydrocoton*, $C_9H_{11}BrO_3$, forms colourless needles, and melts at 99°; and the *dibromo*-derivative, $C_9H_{10}Br_2O_3$, crystallises in white leaflets, and melts at 133°. The compound obtained by oxidising hydrocoton with chromic acid is metadimethoxyquinone, first prepared by Hofmann (compare Ciamician and Silber, *loc. cit.*; Will, Abstr., 1888, 1089). The author's experiments confirm Ciamician and Silber's conclusion, that "hydrocoton" is trimethylphloroglucinol; he finds that when hydrocoton is heated with concentrated hydrochloric acid in a sealed tube at 85°, small quantities of phloroglucinol are obtained together with phloroglucide and *phloroglucan*, $C_6H_4O_2$, a compound which crystallises from water in white needles, and melts at 118°; the chief portion of the product consists, however, of "*triphloroglucinol chloride*," $C_{18}H_3ClO_6 + 2\frac{1}{2}H_2O$, which crystallises in bright orange needles, and is soluble in alkalis and alcohol, but insoluble in water. When boiled with water, *triphloroglucide*, $C_{18}H_{14}O_7 + 2H_2O$, is formed; it is a dark yellow, hygroscopic, crystalline powder.

The compound obtained by methylating hydrocotoïn is benzoylhydrocoton, as Ciamician and Silber have shown. The author has isolated an isomeride, *i-benzoylhydrocoton*, $C_6H_2(OMe)_3{\cdot}COPh$ [$(OMe)_3 : COPh = 1:3:5:2$], during the crystallisation of crude paracotoïn from alcohol; it forms colourless leaflets, and melts at 115°.

A. R. L.

Phenylacridine. By A. Claus and J. Beckenkamp (*J. pr. Chem.*, [2], **48**, 222—225).—The intense yellow prisms of phenylacridine obtained by crystallisation from alcohol, and the colourless leaflets obtained by sublimation, are found to be crystallographically identical. Both belong to the monoclinic system, $a : b : c = 0{\cdot}9915 : 1 : 1{\cdot}0257$; $\beta = 27° 33'$.

E. C. R.

The Aluminium Chloride Synthesis. By H. Biltz (*Ber.*, **26**, 1960—1962).—In carrying out a Friedel-Crafts synthesis with aluminium chloride, it is sometimes better, for instance, in the preparation of triphenylmethane, to use pure chloride prepared from the metal; in other cases, such as the preparation of tetraphenylethane from stilbene dibromide and benzene, a better yield is obtained when the ordinary commercial chloride is used.

C. F. B.

Action of Chloral on Benzene in the presence of Aluminium Chloride. By H. Biltz (*Ber.*, **26**, 1952—1960).—When a mixture of benzene, carbon bisulphide, and chloral is heated with pure aluminium chloride, there are obtained, in addition to tetraphenylethane and diphenyldichlorethylene, two new substances, both in small quantity.

The first of these, *triphenylvinyl alcohol*, $CPh_2{:}CPh{\cdot}OH$, forms silky, tabular, monoclinic crystals, melts at 136°, and is converted by oxidation into benzophenone and benzoic acid, and by the action of sodium ethoxide into diphenylmethane and benzoic acid. The other, which is a *hydrocarbon* (C 94·24, H 5·78 per cent.), forms silky needles melting at 233°, and is converted by oxidation into a substance which melts at 166—167°, and yields colourless crystals.

C. F. B.

Phthaleïnoxime. II. By P. Friedländer and A. Stange (*Ber.*, **26**, 2258—2264; compare this vol., i, 273).—Those phenolphthaleïns which, when dissolved in alkalis, yield salts with formation of a quinone derivative, very easily combine with hydroxylamine. Thus, the intense blue to brownish-violet alkaline solution of the colourless tetrabromophenolphthaleïns, of orthocresolphthaleïn, and of quinol-, catechol-, and orcinol-phthaleïn react very easily with hydroxylamine; whereas the yellow solutions of di- and tetra-nitrophenolphthaleïn do not. The reddish-yellow solution of fluoresceïn, which is very similar to the colour of its salts, and therefore probably contains fluoresceïn of the same constitution, does not react with hydroxylamine. However, the intense violet solution of fluoresceïn and of eosin in concentrated alkali does react with hydroxylamine.

Tetrabromophenolphthaleïnoxime is obtained by treating an alkaline solution of tetrabromophenolphthaleïn with hydroxylamine hydrochloride. It forms amorphous flocks, which cannot be crystallised. When heated in alcoholic solution with dilute sulphuric acid, it yields *dibromoparahydroxyorthobenzoylbenzoic acid* and dibromamidophenol sulphate. The former crystallises from acetic acid in colourless prisms, and melts at 246—248° with decomposition. The latter, when treated with sodium hydrogen carbonate, yields bromoparamidophenol, which melts at 190° with decomposition, and crystallises in slender needles.

Orthocresolphthaleïnoxime, when treated with sulphuric acid in a similar way, yields *methylparahydroxybenzoylbenzoic acid*,

$$COOH\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH,$$

and paramidorthocresol. The former crystallises in needles, and melts at 230° with decomposition. The latter, on account of its instability, cannot be conveniently separated, but is easily converted into its *dibenzoyl* derivative, which crystallises in white, interlacing needles, and melts at 194°. E. C. R.

Condensation Products of Monobasic Acids with Resorcinol. By G. Cohn (*Ber.*, **24**, 2064—2068).—This paper contains a description of the condensation products of resorcinol with benzoic, phenylacetic, and cinnamic acids; a more detailed paper is to be published at a later date. Condensation takes place when the acid is fused with resorcinol in the presence of zinc chloride or phosphoric anhydride.

Resorcinolbenzeïn, previously prepared by Döbner (*Ber.*, **13**, 610), is formed from resorcinol and benzoic acid. It forms an unstable compound with hydrochloric acid, and is readily acted on by bromine. According to the amount of halogen used and the temperature of the bromination, *di-*, *tetra-*, or *penta-bromoresorcinolbenzeïn* is produced. All these substances have been isolated, and are fluorescent colouring matters which dye silk yellowish-red to pure red shades.

Dinitroresorcinolbenzeïn, $\begin{matrix} OH\cdot C_6H_2(NO_2) \\ | \\ O \end{matrix}\!\!>\!CPh\cdot C_6H_2(OH)_2\cdot NO_2$, is formed by the action of fuming nitric acid in the cold on resorcinolbenzeïn. It crystallises in fascicular groups of brittle, reddish-

yellow needles, and deflagrates above 250° without melting. It dyes silk and wool a beautiful orange-yellow. Its brown alkaline solution is coloured red on boiling with an excess of caustic potash.

Resorcinolphenylaceteïn, $\begin{matrix}OH\cdot C_6H_3\\ |\\ O\end{matrix}\!\!>C(CH_2Ph)\cdot C_6H_3(OH)_2$, is prepared from phenylacetic acid, and forms microscopic, brown, rhombic plates melting at 266—268°. It is only slightly soluble in the usual solvents, but dissolves easily in pyridine and similar substances. In alkaline solution, it shows an intense, brilliant, green fluorescence. From such solutions, it is precipitated by carbonic anhydride in yellowish-red flakes. On wool and silk, it produces yellow shades. On heating with acetic anhydride, a *diacetyl* derivative is formed.

Tetrabromoresorcinolphenylaceteïn, $\begin{matrix}C_6HBr_2\\ |\\ O\end{matrix}\!\!>C(CH_2Ph)\cdot C_6HBr_2(OH)_2$, formed by the direct action of bromine, melts at 236°, and closely resembles ordinary eosin prepared from phthalic acid. The *silver salt* is a deep red precipitate.

Tetrabromoresorcinolhydrocinnamyleïn, prepared in a similar manner from hydrocinnamic acid, also very closely resembles eosin in properties. The nature of the eosin produced seems not to depend on the aromatic acid employed, but almost entirely on the brominated phenolic residue. When more complicated aromatic acids are used for the condensation, however, higher brominated substances of a redder shade, which contain bromine in the side chain, can be obtained. Thus, *pentabromoresorcinolphenylaceteïn*, which crystallises in groups of long, red needles, dyes silk a splendid reddish-violet. This substance is more readily soluble in neutral and alkaline solvents than the eosins are, and does not show any trace of fluorescence in alkaline solution.

Tetranitroresorcinolphenylaceteïn is a yellow, indistinctly crystalline powder, which is moderately soluble in alcohol, and dyes wool and silk brown. Its brown alkaline solution, on boiling with an excess of potash, is coloured red in the same way as that of dinitroresorcinolbenzeïn.

Resorcinolcinnamyleïn, prepared from cinnamic acid, is a brown, amorphous mass, which attains a green, metallic lustre at 100°. It is difficult to free it from fluorescent impurities, but, when pure, it forms a red, entirely non-fluorescent solution in alcohol. It dissolves in concentrated sulphuric acid, forming a solution which shows an intense green fluorescence. Hydrogen chloride forms an additive product which is not dissociated by water, and can be obtained in bluish-red matted needles. *Hexabromoresorcinolcinnamyleïn* crystallises in blunt needles, and is slightly soluble in acetic acid, more readily in alcohol, and very readily in alkalis. On heating, it loses hydrogen bromide. It dyes silk a violet-blue, and does not show fluorescence in any of its solutions.

Compounds analogous to resorcinolcinnamyleïn have been prepared from ortho-, meta-, and para-nitrocinnamic acid, as well as from orthohydroxycinnamic acid, but their constitutions have not yet been ascertained. A. H.

Fluoresceïnanilide. By O. Fischer and E. Hepp (*Ber.*, **26**, 2236—2237).—When fluoresceïn is heated with aniline and aniline hydrochloride, *fluoresceïnanilide*, $CO<^{C_6H_4}_{NPh}>C<^{C_6H_3(OH)}_{C_6H_3(OH)}>O$, is obtained; it crystallises from ethylic acetate in plates or flat tablets, which, on heating to 200°, become red, and give a red sublimate. It is readily soluble in glacial acetic acid, but insoluble in water. Its solutions are colourless, and, although it yields colourless solutions with alkalis, the alkaline liquid shows a strong green fluorescence. The solution in concentrated sulphuric acid has a yellowish colour and a faint green fluorescence. The compound is not decomposed by boiling with dilute acids or alkalis, but yields fluoresceïn and aniline when its concentrated alcoholic solution is boiled for some time with 40 per cent. sulphuric acid. Its *dimethyl ether* crystallises from hot alcohol in splendid, colourless, pointed prisms, and melts at 207—208°. Only the sulphuric acid solution of this substance shows any fluorescence. The ether is also very stable towards acids and alkalis.

The formula of the anilide, according to the present views as to the constitution of the fluoresceïns, would be that above; from this point of view, however, it is difficult to understand how the anilide is colourless, whilst fluoresceïn itself is a coloured substance. This may be more easily understood if a quinonoïd formula,

$$COOH\cdot C_6H_4\cdot C<^{C_6H_3(OH)}_{C_6H_3O\text{---}}>O,$$

be given to fluoresceïn itself (compare Armstrong, Proc., 1893, 52).

A. H.

Naphthyl Red and Magdala Red. By O. Fischer and E. Hepp (*Ber.*, **26**, 2235—2236; compare this vol., i, 333, 464, 613).—Naphthyl blue (symmetrical $\alpha\beta$-anildophenylnaphthinduline) is formed by the condensation of benzeneazophenyl-α-naphthylamine when the hydrochloride of the latter is dissolved in phenol and the solution heated (this vol., i, 338). This reaction has been applied by the authors to other azo-compounds. Benzeneazo-α-naphthylamine, when heated with phenol, yields a red colouring matter, strikingly similar in its dyeing power and fluorescence to Magdala red. This compound, $NH{:}C_{10}H_5<^{N\text{---}}_{NPh}>C_{10}H_5\cdot NH_2$, has proved to be the parent substance from which naphthyl violet,

$$NH{:}C_{10}H_5<^{N\text{---}}_{NPh}>C_{10}H_5\cdot NHPh,$$

and naphthyl blue, $NPh{:}C_{10}H_5<^{N\text{---}}_{NPh}>C_{10}H_5\cdot NHPh$, are derived, and has therefore received the name of *naphthyl red*. On treatment with concentrated hydrochloric acid under pressure, it loses ammonia, and an amidonaphthindone is formed, which, on continued treatment, loses a second molecule of ammonia and passes into the same Nt_2-4-hydroxynaphthindone as is formed from naphthyl blue and violet.

Magdala red itself is obtained when amidoazonaphthalene is heated with phenol at 130°, and, on treatment with hydrochloric acid, yields the corresponding indones, $C_{30}H_{19}N_3O$ and $C_{30}H_{18}N_3O_2$. The second of

these dissolves in alkalis, forming red solutions which have a fiery fluorescence. The constitution of Magdala red is therefore

$$NH{:}C_{10}H_5{<}\begin{matrix}N\\N(C_{10}H_7)\end{matrix}{>}C_{10}H_5{\cdot}NH_2,$$

which also shows its relation to naphthyl red.

The details of the investigation will be subsequently published.

A. H.

Phenanthridone. By A. Pictet and E. Patry (*Ber.*, **26**, 1962—1968).—In order to explain the difference between Pictet and Ankersmit's so-called hydroxyphenanthridine (Abstr., 1892, 196) and Graebe and Wander's phenanthridone (this vol., i, 658), the authors were led to study the oxidation of phenanthridine. This base, however, withstands the action of most oxidising agents, but ultimately the following method was adopted. The finely-pulverised phenanthridine (1 gram) was mixed with a 20 per cent. solution of bleaching powder (500 c.c.) and a 10 per cent. solution of cobalt nitrate dropped into the boiling liquid until the reaction ceased, after which the boiling was continued for an hour. The liquid, when cold, was filtered, and the oxidation product isolated from the cobalt oxide by extraction with hot alcohol or, preferably, by sublimation. In this way a compound was obtained melting at 293° (corr.) identical with Graebe and Wander's phenanthridone, so that the nature of Pictet and Ankersmit's compound still remains an open question. Acridine is more advantageously converted into acridone by the method just described than by that of Graebe and Lagodzinski (this vol., i, 649). Pictet and Ankersmit have already shown that when phenanthridine methiodide is treated with alkali, it is converted into a methyl hydroxide. When the latter is oxidised with alkaline ferricyanide solution, *methylphenanthridone*, $\begin{matrix}C_6H_4{\cdot}CO\\C_6H_4{\cdot}NMe\end{matrix}$, is obtained; this crystallises from alcohol in white needles, melts at 108°, and is insoluble in water, dilute acids, and alkalis.

Phenanthridine ethiodide is obtained by heating phenanthridine with ethylic iodide in a sealed tube at 100°; it melts at 253°, and yields the *ethyl hydroxide* melting at 95° when treated with alkalis. By oxidising the latter with alkaline ferricyanide, *ethylphenanthridone*, $\begin{matrix}C_6H_4{\cdot}CO\\C_6H_4{\cdot}NEt\end{matrix}$, melting at 88°, is formed.

Benzylphenanthridone, $\begin{matrix}C_6H_4{\cdot}CO\\C_6H_4{\cdot}N{\cdot}CH_2Ph\end{matrix}$, is obtained by heating phenanthridine with benzylic chloride, treating the *phenanthridine benzyl chloride* so prepared with alkali, and oxidising the resulting *hydroxide* with alkaline ferricyanide; it forms small, white leaflets, and melts at 115°.

A. R. L.

Orientation in the Terpene Series. By A. Baeyer (*Ber.*, **26**, 2267—2271; this vol., i, 359).—A *tertiary menthol* is obtained by treating menthene with a solution of hydrogen iodide or bromide in acetic acid cooled with ice, and then decomposing the pure halogen

derivative dissolved in acetic acid with silver acetate. The *acetate* obtained in this way is separated from menthene by distillation in a vacuum and hydrolysed. The alcohol boils at 97—101° under 20 mm. pressure, has a faint odour of peppermint, and solidifies to a vitreous mass when cooled with solid carbonic anhydride. It behaves as a tertiary alcohol towards chromic acid and halogen hydrides. The *bromide* prepared from it, when heated with quinoline, yields menthene (b. p. 167·5°).

Tertiary carvomenthol, obtained from carvomenthene in a similar way, boils at 96—100° under 17 mm. pressure, is similar to the tertiary menthol, and when its bromide is heated with quinoline yields carvomenthene (b. p. 174·5°).

Tertiary menthylamine is obtained by treating the tertiary iodide or bromide obtained from menthene in ethereal solution with silver cyanate and hydrolysing the oil thus produced with alkali. The *hydrochloride* melts at 205°. The *platinochloride* crystallises in leaflets, and decomposes at 235°. The *phenylthiocarbamide* crystallises in radiating leaflets, and melts at 118—119°. The *benzoyl compound* crystallises in needles, and melts at 154·5°.

Tertiary carvomenthylamine is obtained in a similar way. The *hydrochloride* is a syrup which slowly crystallises. The *phenylthiocarbamide* crystallises in prisms, and melts at 128°. The *benzoyl compound* crystallises in large needles and melts at 110°. E. C. R.

Carvole. By H. Goldschmidt (*Ber.*, **26**, 2084—2087).—γ-Carvoxime, on reduction with sodium amalgam, or zinc dust and acetic acid, yields carvylamine, $C_{10}H_{17}N$, not the dihydrogen derivative as assumed by Wallach (Abstr., 1892, 499); the previous observations of Goldschmidt and Kisser are, therefore, confirmed. The amine boils at 98—99° under a pressure of 10 mm., and consists of two stereoisomerides which can be separated by the fractional crystallisation of their benzoyl derivatives. The α-modification, $C_{10}H_{16}NBz$, is sparingly soluble in benzene, and crystallises in long, slender, colourless needles, melting at 168—169°. The corresponding *α-carvylphenylcarbamide*, $C_{10}H_{15}\cdot NH\cdot CO\cdot NHPh$, melts at 187—191°, and could not be completely freed from the β-derivative. *β-Carvylamine nitrate* is less soluble than the corresponding α-salt; the *benzoyl derivative*, $C_{10}H_{15}\cdot NHBz$, crystallises in long, transparent plates, melting at 103°. *β-Carvylphenylcarbamide* is deposited in small, colourless needles, melting at 138°. The formula $C_{10}H_{15}NO$ for isocarvoxime (m. p. 143—144°) is confirmed, its molecular weight having been determined by means of the boiling point method, using ether as solvent; it is optically inactive, and by the action of dilute sulphuric acid is resolved into hydroxylamine, carvacrole, and carvoline. The carvacrole was identified by means of the phenyl cyanate derivative, which is deposited from light petroleum in long, transparent needles, melting at 134—135°. Carvoline, which is isomeric with carvacol, melts at 94°, and is probably a secondary base.

Carvacrylamine, $NH_2\cdot C_6H_3Me,Pr^a$ [= 1 : 2 : 5], is formed by the reduction of isocarvoxime in alcoholic solution with zinc dust and acetic acid, and is identical with the compound obtained by the action of zinc ammonium chloride on carvacrole: the acetyl derivative melts at

71°, and not at 115°, as stated by Lloyd. The yield of carvacrylamine was 44 per cent. of the theoretical. By the reduction of isocarvoxime with zinc dust in glacial acetic acid solution, carvacrylamine and carvoline are obtained; the latter is probably derived from the former by rearrangement (Beckmann's reaction). Isocarvoxime on reduction with sodium and alcohol, yields carvacrylamine, carvoline, and a hydrogenised base which is being further investigated. J. B. T.

Isomeric Menthylamines. By O. Wallach and M. Kuthe (*Annalen*, **276**, 296—314).—Representing menthone by the formula $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CO}>CH\cdot C_3H_7$, it is seen to contain two asymmetrical carbon atoms. When the carbonyl group is converted into the group $CH\cdot NH_2$, a third carbon atom is rendered asymmetrical, and the production of optical isomerides becomes possible. Now, it has been previously shown (*Ber.*, **25**, 3313) that by reducing *l*-menthoneoxime (see also Andres and Andreef, Abstr., 1892, 723), a lævorotatory menthylamine is formed, whilst the base prepared from menthone and ammonium formate consists mainly of a dextrorotatory compound together with some of the lævorotatory isomeride. That these two isomerides do not rotate the plane of polarised light in opposite directions to an equal extent is what might be expected, for if the optical function of the two asymmetrical carbon atoms in *l*-menthone experiences no alteration by the appearance of a third, the two isomeric menthylamines which might theoretically be formed cannot possibly have equal rotatory powers in opposite directions. The two isomerides are distinguished as *l*- and *r*-menthylamine, and inasmuch as they exhibit many analogies with the hydrogenised phthalic acids, they may be regarded as cis- and trans- forms respectively.

A yield of *l*-menthylamine, $C_{10}H_{19}\cdot NH_2$, amounting to 90 per cent. of the theoretical is obtained when lævomenthone is dissolved in absolute alcohol, and the solution boiled with sodium; it boils constantly at 205°. The *hydrochloride* is a snow-white powder which does not melt at 280°, and the *hydrobromide* crystallises in needles and becomes brown at 200°. The *formyl* derivative, $C_{10}H_{19}\cdot NH\cdot COH$, melts at 102—103°; the *acetyl* derivative melts at 145°, the *propionyl* derivative at 89°, and the *butyryl* derivative at 80°. *l-Phenylmenthylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{19}$, is prepared by treating an ethereal solution of *l*-menthylamine with phenylthiocarbimide; it forms lustrous crystals, and melts at 135°. *l-Benzylidenementhylamine*, $C_{10}H_{19}\cdot N{:}CHPh$, is obtained by treating a methyl alcoholic solution of *l*-menthylamine with benzaldehyde; it melts at 69—70°. The *orthohydroxybenzylidene* derivative melts at 56—57°.

When lævomenthone is heated with ammonium formate at 190—200°, the product is a mixture of *r*- and *l*-formylmenthylamine. *r*-Menthylamine is obtained by boiling the formyl derivative with alcoholic potash; it has the same boiling point as *l*-menthylamine, but the derivatives of the two differ in melting point and solubility (see also above). The *hydrochloride* crystallises in tables, and melts at 189°; the *hydrobromide* melts at 225°; and the *hydriodide* melts at 270° with decomposition. *r-Formylmenthylamine*, $C_{10}H_{19}\cdot NH\cdot COH$,

melts at 117·5°; the *acetyl* derivative, $C_{10}H_{19}\cdot NHAc$, melts at 168—169°, the *propionyl* derivative at 151°, and the *butyryl* derivative at 105—106°.

r-Phenylmenthylthiocarbamide, $NHPh\cdot CS\cdot NHC_{10}H_{19}$, melts at 178—179°; *r-allylmenthylthiocarbamide*, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_{10}H_{19}$, melts at 110°; *r*-benzylidenementhylamine crystallises in lustrous needles, and melts at 42—43°; its *orthohydroxy*-derivative melts at 96—97°.

The author finds that when lævomenthone is treated with concentrated sulphuric acid in the manner described by Beckmann (Abstr., 1889, 722), a certain amount is converted into dextromenthone.

A. R. L.

Optical Rotatory Powers of certain Compounds of the Fenchylamine and Menthylamine Series. By O. Wallach and A. Binz (*Annalen*, **276**, 315—327).—The following table contains the mean values obtained for the specific and molecular rotatory powers of fenchone and its derivatives in chloroform solutions.

	Melting point.	$[\alpha]_D$.	$[M]_D$.
Fenchonoxime	165·0°	+52·44°	+87·40°
Fenchylamine	—	−24·89	−38·00
Formylfenchylamine	114·0	−36·56	−66·04
Acetylfenchylamine	99·0	−46·62	−90·73
Propionylfenchylamine	123·0	−53·16	−110·88
Butyrylfenchylamine	77·5	−53·11	−118·19
Benzylidenefenchylamine	42·0	+73·14	+175·90
Orthohydroxybenzylidenefenchylamine.	94·0	+66·59	+170·77
Parahydroxybenzylidenefenchylamine..	175·0	+72·00	+184·65
Orthomethoxybenzylidenefenchylamine	56·0	+59·20	+160·09
Paramethoxybenzylidenefenchylamine .	55·0	+78·05	+211·07

The values for the rotatory powers of the ortho- and para-hydroxybenzylidene derivatives show that the alteration in the rotatory power of active substances by the introduction of a radicle is not, as Guye supposes (*Arch. Sci. phys. nat.*, 1891, 97), a function of the molecular weight of that radicle.

The optical investigation of derivatives of *l*- and *r*-menthylamine

	$[\alpha]_D$.	Diff.	$[M]_D$.	Diff.
l-Formylmenthylamine	−83·37°		−152·27°	
		1·56		8·57
l-Acetylmenthylamine	−81·81		−160·84	
		5·28		0·31
l-Propionylmenthylamine	−76·53		−161·15	
		4·43		0·75
l-Butyrylmenthylamine	−72·10		−160·90	
r-Formylmenthylamine	+54·03		+98·68	
		3·46		0·74
r-Acetylmenthylamine	+50·57		+99·42	
		5·43		4·37
r-Propionylmenthylamine	+45·14		+95·05	
		4·55		3·91
r-Butyrylmenthylamine	+40·59		+91·14	

(last abstract) seemed particularly adapted to elucidate the question whether analogous compounds having common differences exhibit any regularity in the alteration of their rotatory powers. It is seen by the preceding table (p. 725) that this is not the case. The compounds were examined in chloroform solutions.

A somewhat striking regularity is exhibited by comparing the similar derivatives of the two series, thus.

	$[\alpha]_D$.	Diff.
l.-Formylmenthylamine	−83·37°	29·34
r.-Formylmenthylamine	+54·03	
l.-Acetylmenthylamine	−81·81	31·24
r.-Acetylmenthylamine	+50·57	
l.-Propionylmenthylamine	−76·53	31·39
r.-Propionylmenthylamine	+45·14	
l.-Butyrylmenthylamine	−72·10	31·51
r.-Butyrylmenthylamine	+40·59	

A. R. L.

Essence of Eucalyptus globulus. By E. Spizzichino (*L'Orosi*, **16**, 1—6).—50 kilos. of the dried leaves of *Eucalyptus globulus* yield on distillation about 600 grams of oil. On prolonged boiling with alcoholic soda, the essence loses its characteristic odour, and acquires that of camphor, whilst the soda solution probably retains acetic and valeric acids, resulting from the hydrolysis of some constituents of the essence. The oil, purified by this means, boils principally at 170—180°; the fraction boiling at 170—175°, when treated with barium oxide and fractionated, gives pure eucalyptol, $C_{10}H_{18}O$, boiling at 171—173°. It has a camphor-like odour, does not react with phenylhydrazine or hydroxylamine, and is but slightly acted on by sodium.

On heating a mixture of eucalyptol and metanitrobenzaldehyde in molecular proportion with a little dilute sulphuric acid, vigorous action occurs. The friable mass obtained on cooling, when purified by the method employed by Bertoni in similar cases (Abstr., 1891, 1378), yields *metanitrophenoleucalyptolmethane*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}C_{10}H_{16}O$, as a reddish, amorphous powder; it is soluble in chloroform, acetone, ethylic acetate, and benzene, but insoluble in water or light petroleum. On heating, it softens and explodes slightly with evolution of yellow vapours. W. J. P.

Essence of Eucalyptus. By G. Bouchardat and Oliviero (*Bull. Soc. Chim.*, [3], **9**, 429—432).—The essence of eucalyptus contains aldehydes—valeraldehyde with a little hexylaldehyde and, in some samples, butaldehyde; alcohols—mainly ethyl and amyl (mostly inactive) alcohols, eucalyptol, and a lævorotatory substance $C_{20}H_{18}$, together with a dextrorotatory substance of higher boiling point. The examination of the latter substances is proceeding. W. T.

Essence of Niaouli. By G. Bertrand (*Bull. Soc. Chim.*, [3], **9**, 432—437).—The essence of niaouli contains:—(1), in small quantity, volatile fatty acids, especially valeric acid, a substance which may be methylic salicylate, a thio-compound, ethereal salts of terpilenol, and benzaldehyde with a trace of valeraldehyde; (2) as principal constituents, a dextrorotatory turpentine, inactive eucalyptol boiling at 175° (forming two-thirds by weight of the essence), a lævorotatory citrene boiling at 175°, and terpilenol boiling at 218°.

W. T.

Anemonin and its Occurrence. By W. K. J. Schoor (*Chem. Centr.*, 1893, ii, 60; from *Maandbl. natuurw.*, **18**, 23—40).—Anemonin occurs in many of the *Ranunculaceæ*; it is a toxic substance, and produces paralysis of the central nervous system. The compound has the formula $C_{15}H_{12}O_6$, and is deposited in rhombic crystals melting at 152°. It is volatile with steam, and on exposure to air at ordinary temperatures is slowly converted into anemonic acid; the oxidation proceeds more quickly if platinum black, hydrogen peroxide, or barium peroxide is employed.

J. B. T.

Crystalline Acid from Lichen (Thamnolic acid). By W. Zopf (*Chem. Centr.*, 1893, ii, 54—55; from *Hedwigia*, 1893, 66—69).—The author has prepared, from *Thamnolia vermicularis*, a compound which he proposes to term *thamnolic acid*, to the presence of which the plant owes its light colour. The lichen is extracted with dilute soda, the solution acidified with hydrochloric acid, and the precipitate crystallised from methyl alcohol; it melts at 202—204° with decomposition.

J. B. T.

Valency of Nitrogen in Pyrroline. By E. Bamberger (*Ber.*, **26**, 1946—2947).—A reply to Ciamician and Zanetti (this vol., i, 602).

Amido- and Nitro-derivatives of Pyridine. By W. Marckwald (*Ber.*, **26**, 2187—2189).—2-Chloropyridine will not exchange its chlorine for amidogen, but chloronicotinic acid [Cl : COOH = 2 : 5] does, when heated with strong aqueous ammonia at 170°. The product, *amidonicotinic acid* [NH_2 : COOH = 2 : 5], forms minute crystals which melt above 300°; when heated, it loses carbonic anhydride, and yields 2-*amidopyridine*, which melts at 56°, and boils at 204°. When amidonicotinic acid is dissolved in strong sulphuric acid and the theoretical quantity of strong nitric acid added, *nitramidonicotinic acid* [NO_2 : NH_2 : COOH = 3 : 2 : 5 probably] is obtained; it forms small, yellow crystals which melt at about 280°.

C. F. B.

Amido-derivatives of Quinoline. III. By J. Ephraim (*Ber.*, **26**, 2227—2230; compare Abstr., 1891, 1509; 1892, 1498).—γ-Chloroquinaldine reacts with phenylhydrazine at 115° yielding *phenylhydrazo-γ-quinaldine*, $C_9NH_5Me{\cdot}NH{\cdot}NHPh$, which forms yellowish white crystals melting at 134—135°. This substance has strongly

basic properties, and gives a *hydrochloride* which melts at 272° with decomposition.

γ-Amidoquinaldine is obtained by the reduction of the foregoing compound, and forms beautiful white needles melting at 168°. The *platinochloride* of the base melts at 228°.

It has been shown that in the quinoline ring a chlorine atom in the *α*- or *γ*-position will react with bases, whilst if in the *β*-position no reaction takes place even on continued heating. This reaction may, therefore, be used as a means of ascertaining the constitution of halogen derivatives of quinoline. Thus, kynurenic acid may be converted by loss of carbonic anhydride into kynurin, from which a chloroquinoline can be prepared. This substance, when heated with aniline, enters into reaction, and yields a *phenylamidoquinoline* melting at 198°. The chloroquinoline, which is undoubtedly different from the *α*-compound, must therefore be *γ*-chloroquinoline, and the position of the hydroxyl group in kynurin and kynurenic acid is also thus determined.

γ-Chlorocarbostyril forms an exception to the general rule as stated above. In order to ascertain the reason of this exceptional behaviour, this substance was converted by the action of phosphorus pentachloride into *αγ*-dichloroquinoline, and the latter heated with aniline. A reaction takes place, and *αγ-dianilidoquinoline*,

$$C_9NH_5(NHPh)_2,$$

melting at 149°, is formed. *α*-Ethoxy-*γ*-chloroquinoline also reacts with aniline yielding *α-ethoxy-γ-phenylamidoquinoline*, which crystallises from alcohol in white needles, and does not melt below 270°.

The stability of the chlorine atom of *γ*-chlorocarbostyril towards bases seems, therefore, to be due to the presence of the hydroxyl group. A. H.

Alkyl and Alkylene Derivatives of Substituted Cinchonic acids. By A. Claus (*Annalen*, **276**, 266—267).—General and introductory remarks on the papers following.

Alkyl Derivatives of Quininic acid. By A. Claus and F. Stohr (*Annalen*, **276**, 267—281).—When quininic acid is heated with an excess of methylic iodide in a sealed tube at 130°, the *methiodide*, $OMe{\cdot}C_9NH_5{\cdot}COOH,MeI$, is obtained; it forms yellow, lustrous needles, melts at 205° with decomposition, and is soluble in boiling water and alcohol. The *methochloride* melts at 215°. The *sulphate*,

$$(OMe{\cdot}C_9NH_5{\cdot}COOH)_2,Me_2SO_4,$$

obtained by treating the methohalogen compounds with silver sulphate, melts at 245°; and the nitrate, $OMe{\cdot}C_9NH_5{\cdot}COOH,MeNO_3$, formed by treating them with silver nitrate, melts at 192°.

Quininicacid methylbetaïne, $OMe{\cdot}C_9NH_5Me<\begin{matrix}CO\\|\\C\end{matrix}$, is obtained by treating a cold aqueous solution of either of the last-described methohalogen compounds with moist silver oxide, or by treating the methosulphate with barium hydroxide; it crystallises in tufts of

yellow needles, melts at 194° with decomposition, and is readily soluble in water, but insoluble in ether; the salts formed by the action of acids are identical with those obtained from the methohalogen derivatives of quininic acid and silver salts.

Methyleneparamethoxycinchoxinic acid,

$$O<\begin{matrix}CH_2\cdot N:C_9H_5(OMe)\cdot COOH\\ |\\ CH_2\cdot N:C_9H_5(OMe)\cdot COOH'\end{matrix}$$

is formed by treating the metho-salts, above described, with moderately dilute potash, and adding a slight excess of dilute acid to the red solution; the precipitate, in the freshly precipitated, moist condition, is readily soluble in ether, but loses its solubility when dried; it is an intensely yellow powder, melts at 282°, has no basic properties, and is soluble in alcohol, but only very sparingly in water. The *silver* salt is a grey precipitate, and the *copper* salt is a dark green precipitate.

Quininic acid ethobromide, $OMe\cdot C_9NH_5\cdot COOH,EtBr$, melts at 210°, and the *propobromide* at 192°. *Quininic acid benzylobromide*, $OMe\cdot C_9NH_5\cdot COOH,CH_2PhBr$, is obtained by heating quininic acid and benzylic bromide in a sealed tube at 130°; it crystallises from alcohol in yellow, lustrous needles, melts at 149° with decomposition, and is sparingly soluble in water, insoluble in ether, chloroform, and benzene. When treated with silver oxide, it gives the *benzylbetaïne* $C_{18}H_{15}NO_3$; this crystallises in tufts of prisms having the colour of topaz, and melts at 159°. *Benzylideneparamethoxycinchoxinic acid*, $O<\begin{matrix}CHPh\cdot N:C_9H_4(OMe)\cdot COOH\\ |\\ CHPh\cdot N:C_9H_4(OMe)\cdot COOH'\end{matrix}$, is obtained by treating the benzylbetaïne with moderately concentrated alkalis, and acidifying the solution; it crystallises from alcohol in lustrous, transparent needles, and melts at 270°; the *silver* salt is a brownish-yellow powder, and the *copper* salt a bright green powder. A. R. L.

Pyrazines and Piperazines. By L. Wolff (*Ber.*, **25**, 1923—1925).—A reply to Stoehr (this vol., i, 612), who has questioned the accuracy of certain data and opinions published by the author.

Derivatives of Pyrazolone. By R. v. Rothenburg (*Ber.*, **26**, 2053—2059; compare Abstr., 1893, i, 180).—*Pyrazolone*,

$$NH<\begin{matrix}N=CH\\ |\\ CO\cdot CH_2\end{matrix}'$$

is less stable than its derivatives; on treatment with concentrated hydrochloric acid, a salt is first formed, but is rapidly decomposed into humus-like substances. Nitrous acid converts it into an *isonitroso-compound*, $NH<\begin{matrix}N=CH\\ |\\ CO\cdot C:NOH\end{matrix}'$, which crystallises in reddish-yellow needles melting at 87°, and is decomposed by an excess of nitrous acid.

Pyrazolone-3-carboxylic acid, $NH<\begin{matrix}N=C\,COOH\\ CO\cdot CH_2\end{matrix}$, is formed in very small quantity by the oxidation of 3-methylpyrazolone, as well as by the ordinary method of preparation (Abstr., 1893, i, 180). It forms crystalline salts of *sodium*, *ammonium*, and *copper*. The free acid decomposes on heating, whereas the ethylic salt may be distilled without decomposition. On heating the calcium salt, pyrazolone is formed, together with 3-*dipyrazoloneketone*, $\left(\begin{matrix}NH-N\\ CO\cdot CH_2\end{matrix}>C\right)_2CO$, which is a thick, yellow oil, is very sensitive to light, and boils at 203—204°. It reacts with phenylhydrazine acetate to form 3-*dipyrazolonemethylenephenylhydrazone*, $\left(\begin{matrix}NH-N\\ CO\cdot CH_2\end{matrix}>C\right)_2C{:}N\cdot NHPh$, which melts at 113°. *Methylic pyrazolonecarboxylate*, $\begin{matrix}NH-N\\ CO\cdot CH_2\end{matrix}>C{:}COOMe$, may be prepared from methylic oxalacetate or methylic acetylenedicarboxylate by the action of hydrazine hydrate, or by the etherification of pyrazolonecarboxylic acid with methyl alcohol and hydrochloric acid; it forms yellow crystals melting at 226·5—227·5°. The *amide* is an indistinctly crystalline mass melting with decomposition at 219°.

Methylic 4-benzalpyrazolone-3-carboxylate, $NH<\begin{matrix}N=C\cdot COOMe\\ CO\cdot C{:}CHPh\end{matrix}$, is a sparingly soluble powder melting above 250°.

Methylic 4-azobenzenepyrazolone-3-carboxylate, $NH<\begin{matrix}N=C\cdot COOMe\\ CO\cdot C{:}N\cdot NHPh\end{matrix}$, which is prepared by the action of diazobenzene sulphate, crystallises from alcohol in fiery-red crystals melting at 209—211°, and has acid properties.

Methylic 4-isonitrosopyrazolone-3-carboxylate, $NH<\begin{matrix}N=C\cdot COOMe\\ CO\cdot C{:}NOH\end{matrix}$, is prepared by the action of nitrous fumes on an alcoholic solution of the methylic salt. It crystallises in yellowish-red granules, melts at 199—201°, and is a strong acid. It forms deep-red solutions with alkalis, and yields a red, granular *silver salt*, which detonates when rapidly heated. When its alcoholic solution is treated with hydrazine hydrate, 4-*hydrazipyrazolone-3-carbonylhydrazine*, $NH<\begin{matrix}N=C\cdot CO\cdot NH\cdot NH_2\\ CO\cdot C{:}N\cdot NH_2\end{matrix}$, is produced; this melts above 250°, and loses hydrazine when boiled with acids or alkalis. On treatment with benzaldehyde, it yields 4-*benzalazipyrazolone-3-carbonylbenzalhydrazine*, $NH<\begin{matrix}N=C\cdot CO\cdot NH\cdot N{:}CHPh\\ CO\cdot C{:}N\cdot N{:}CHPh\end{matrix}$, which forms yellow needles melting at 217·5°.

When 4-isonitrosopyrazolone-3-carboxylic acid is treated with excess of hydrazine hydrate, the *lactam of 4-hydrazipyrazolonecarboxylic acid*, $NH<\begin{matrix}N=C\cdot CO\\ CO\cdot C=N\end{matrix}>NH$, is produced. This compound

crystallises from dilute hydrochloric acid in white granules, decomposing at 125—126°; it does not give a benzal compound on treatment with benzaldehyde, or yield hydrazine on boiling with alkalis or acids. It probably exists in the lactim form in its intensely coloured, reddish-yellow alkaline solution.

Attempts to prepare derivatives of pyrazolone by the action of hydrazine hydrate on ethylic anilidoacrylate and ethylic cinnamate, by the abstraction of water from tartrylhydrazine, and by the action of ammonia on phenyloxazolone, proved unsuccessful. Phenyloxazolone was, however, converted into 3-phenylpyrazolone, $\begin{matrix}NH—N\\ \vert \quad \quad >CPh\\ CO\cdot CH_2\end{matrix}$, by the action of hydrazine hydrate.

Tartrylhydrazine, $NH_2\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH\cdot NH_2$, is slightly soluble in alcohol, readily in water, and forms delicate, matted needles melting at 182·5—183°. *Tartrylbenzalhydrazine*, $C_2H_2(OH)_2\cdot(CO\cdot NH\cdot N{:}CHPh)_2$, forms yellowish plates, and melts at 225°. A. H.

Alkyl Derivatives of 2′-Phenylcinchonic acid. By A. Claus and B. Büttner (*Annalen*, **276**, 282—295).—*2′-Phenylcinchonic acid methiodide*, $C_6H_4<\begin{matrix}C(COOH)\cdot CH\\ \vert \quad \quad \vert \\ N(MeI)—CPh\end{matrix}>$, is obtained by heating cinchonic acid with methylic iodide in a sealed tube at 130°. It crystallises from alcohol in lustrous, copper-coloured scales, and separates, on the addition of ether to the alcoholic solution, in orange-red needles; it melts at 182—186° with decomposition. The *methochloride* forms yellowish prisms, becomes green below 140°, and melts at 209—210° with decomposition. The *methosulphate* crystallises in rhombic prisms.

2′-Phenylcinchonic acid methylbetaïne, $C_9NH_5MePh<\begin{matrix}CO\\ \vert \\ O\end{matrix}>$, is formed when moist silver oxide is added to an aqueous alcoholic solution of the methiodide; it separates from its alcoholic solution in large, yellow, rhombic tables, becomes green at 100°, and melts at 220—221° with decomposition. The salts obtained on treating the methylbetaïne with acids are identical with those formed by the action of silver salts on 2′-phenylcinchonic acid methiodide.

The methylbetaïne combines with methylic iodide when heated with it in a sealed tube at 100°, forming a *methiodide*,

$$C_9NH_5Ph\cdot COOMe,MeI,$$

which crystallises from water in small, garnet-red needles, and melts at 160—161° with decomposition. When the methylbetaïne is dissolved in alkali and the solution cautiously acidified with hydrochloric acid, 2′-phenylcinchonic acid methochloride is obtained, but if the alkaline solution is evaporated, the residue redissolved in water, and the solution acidified with hydrochloric acid, a dark-coloured oxidation product is obtained. Further experiments are in progress.

A. R. L.

Pyridazolone. By R. v. Rothenburg (*Ber.*, **26**, 2061—2064).—Ethylic succinoformate, $COOEt\cdot CO\cdot CH_2\cdot CH_2\cdot COOEt$, reacts with hydrazine hydrate in a similar manner to ethylic oxalacetate (Abstr., 1893, i, 180), the product being *ethylic pyridazolone-3-carboxylate*, $CO<^{NH-N}_{CH_2\cdot CH_2}>C\cdot COOEt$. This substance dissolves very readily in all solvents, and crystallises with difficulty in granules melting at 171·5—172°. It yields precipitates with silver nitrate and copper sulphate solutions, and does not react with nitrous acid or the salts of diazobenzene to form nitroso- or azo-compounds. On heating with hydrazine hydrate, it is converted into *pyridazolone-3-carbonylhydrazine*, $CO<^{NH-N}_{CH_2\cdot CH_2}>C\cdot CO\cdot NH\cdot NH_2$, which forms very soluble granular crystals melting at 250°. On treatment with benzaldehyde, the carbonylhydrazine yields *pyridazolone-3-carbonylbenzylhydrazine*,

$$CO<^{NH-N}_{CH_2\cdot CH_2}>C\cdot CO\cdot NH\cdot N:CHPh,$$

which separates from alcohol in white flakes melting above 250°.

Ethylic pyridazolonecarboxylate is rapidly decomposed by acids into hydrazine and succinoformic acid, but if alkalis are employed a small quantity of the free *pyridazolone-3-carboxylic acid* is also formed. This is only slightly soluble in water, and forms an indistinctly crystalline mass melting with decomposition above 250°. It yields an amorphous *silver salt*, and a crystalline *calcium salt*. When the latter is distilled with soda lime, a brown oil is produced, consisting of impure pyridazolone, $CO<^{NH-N}_{CH_2\cdot CH_2}>CH$. This substance has not yet been obtained quite pure; it boils at 165—172°, and has an intense odour resembling those of pyridine and pyrazolone. Acids and alkalis decompose it with formation of hydrazine.

A. H.

Phthalazine. By S. Gabriel and G. Pinkus (*Ber.*, **26**, 2210—2216).—*Phthalazine*, $C_6H_4<^{CH}_{CH}>N_2$, may be prepared by heating tetrachlorortho-xylene, $C_6H_4(CHCl_2)_2$, with aqueous hydrazine at 150°, or, better, by converting it into phthalaldehyde and hydrochloric acid by boiling with water, and then adding potash and hydrazine sulphate, and concentrating, so as to complete the reaction $C_6H_4(CHO)_2 + 4HCl + 5KOH + N_2N_4.H_2SO_4 = C_8H_6N_2,HCl + 3KCl + K_2SO_4 + 7H_2O$. It crystallises in yellowish needles, melts at 90—91°, and boils with partial decomposition at 315—317°; the *hydrochloride* forms needles melting at 231° with decomposition, the *platinochloride* brownish-yellow needles melting above 260°, and the *picrate* a crystalline precipitate melting at 208—210°. When phthalazine is reduced with zinc and hydrochloric acid, the nitrogen ring is broken, and orthoxylylenediamine, $C_6H_4(CH_2\cdot NH_2)_2$, is formed (compare Strassman, Abstr., 1888, 474. Ortho-xylylenediphthalimide and dibenzoylortho-xylylenediamine melt at 265—266°

and 184° respectively, not at 253° and 168°). *Diphenylsulphoneortho-xylylenediamine*, $C_6H_4(CH_2{\cdot}NH{\cdot}SO_2Ph)_2$, prepared from the diamine, benzene sulphochloride, and soda, forms colourless plates melting at 127°. Ortho-xylylenediamine was also converted into the imino (dihydroisoindole) by heating its hydrochloride. When phthalazine hydrochloride is reduced with sodium amalgam, the nitrogen ring remains intact, and *tetrahydrophthalazine*, $C_6H_4<\begin{matrix}CH_2{\cdot}NH\\CH_2{\cdot}NH\end{matrix}$, is formed. This is an unstable oil with reducing properties; its *hydrochloride* $C_8N_2H_{10},HCl$ forms long, silky needles melting at 231° with decomposition; the *picrate* melts with decomposition at 159—160°; the *dibenzoyl derivative* forms needles which melt at 207—208°. The action of nitrous acid on the tetrahydro-compound yields an unstable (? dinitroso-) derivative, which decomposes in ethylic acetate solution, evolving nitrogen and forming a substance, $C_8H_6N_2O_2$, ? phthaldialdoxime, $C_6H_4(CH{:}NOH)_2$. This crystallises in lustrous, colourless prisms, and is not very stable; when treated with methylic iodide and sodium methoxide, it yields a colourless, crystalline substance, $C_9H_9N_2O$ (? $CN{\cdot}C_6H_4{\cdot}CH{:}NOMe$), melting at 62—63°.

C. F. B.

Phenazones. By L. Meyer, Jun. (*Ber.*, **26**, 2238—2242).—Orthodinitroditolyl, obtained by the nitration of orthotolidine, behaves towards reducing agents in a similar manner to orthodinitrodiphenyl (Täuber, Abstr., 1892, 183), phenazone derivatives being produced.

Ditolyleneazone or *tolazone*, $\begin{matrix}N{-}C_6H_3Me\\\|\quad\quad|\\N{-}C_6H_3Me\end{matrix}$ [$N_2 : Me_2 = 6 : 6' : 3' : 3$], is formed by the action of sodium amalgam on an alcoholic solution of dinitroditolyl. It crystallises from alcohol in lustrous, yellow prisms, melts at 187° to a greenish-yellow liquid, and boils above 360° almost without decomposition. It is insoluble in water, readily soluble in alcohol, and very readily in benzene. It dissolves in acids with formation of unstable salts; the *hydrochloride* forms dark brown crystals, and the *platinochloride* is only slightly soluble in water. *Tolazone dioxide*, $C_{14}H_{12}N_2O_2$, is formed, along with a small amount of the monoxide, when dinitroditolyl is reduced by means of potash and zinc dust. It crystallises in lustrous, straw-yellow plates which melt at 128° with decomposition.

Diamidotolazone, $\begin{matrix}N{-}C_6H_2Me{\cdot}NH_2\\\|\quad\quad\quad\quad|\\N{-}C_6H_2Me{\cdot}NH_2\end{matrix}$ [$(NH_2)_2 = 4 : 4'$], is formed by the reduction of metadinitrorthotolidine by means of sodium amalgam. It forms dark red crystals melting with decomposition at 276°. It is readily soluble in alcohol, less readily in ether and benzene. The base is capable of forming several series of salts; thus, when it is dissolved in the smallest possible amount of hydrochloric acid, an olive-coloured solution is obtained, which, on the addition of more acid, changes to red.

Diamidotolazone reacts with benzaldehyde to form a *benzylidene* compound, $C_{28}H_{22}N_4$, which is obtained in yellow, lustrous crystals melting with decomposition at 239°.

Methylphenazonecarboxylic acid, $\begin{matrix}N—C_6H_3\cdot COOH\\ \|\\ N—C_6H_3Me\end{matrix}$, is obtained by the oxidation of tolazone with chromic acid. It forms light yellow needles, which undergo no alteration at 290°. The salts of the alkali metals are soluble in water, whilst those of zinc and cadmium are only very slightly soluble.

Attempts to prepare phenazonedicarboxylic acid have hitherto proved unsuccessful. A. H.

Amidoketones. By S. Gabriel and G. Pinkus (*Ber.*, **26**, 2197—2209).—*Amidoacetone*, $COMe\cdot CH_2\cdot NH_2$, may be prepared by boiling acetonylphthalimide, $COMe\cdot CH_2\cdot N:C_8H_4O_2$, with 20 per cent. hydrochloric acid, or, better, by reducing isonitrosoacetone, $COMe\cdot CH:NOH$, in acid solution by means of stannous chloride, tin, and hydrochloric acid, or by zinc and acetic acid. The base itself cannot be obtained pure; it reduces Fehling's solution in the cold. The *hydrochloride* forms a fibrous, deliquescent, crystalline mass; the *platinochloride*, $(C_3H_7NO)_2,H_2PtCl_6$, yellow needles which melt with decomposition at 188—189°; and the *sodium picrate*, $C_3H_7NO,C_6H_3N_3O_7,C_6H_2N_3O_7Na + H_2O$, short prisms melting at 171—173°. The hydrochloride, when treated with phenylhydrazine and sodium acetate at 50°, yields methylphenylglyoxalosazone, $N_2HPh:CMe\cdot CH:N_2HPh$ (Japp and Klingemann, Trans., 1888, 531). With potassium thiocyanate on the water bath, it yields *methylimidazolyl-μ-mercaptan*,

$$\begin{matrix}CMe\cdot NH\\ \|\\ CH—N\end{matrix}\!\!>C\cdot SH;$$

this crystallises in yellowish needles, melts at 242—245°, and is oxidised by hot 10 per cent. nitric acid to *methylimidazole*, $\begin{matrix}CMe\cdot NH\\ \|\\ CH—N\end{matrix}\!\!>CH$, which is an oil boiling at 263° under 764 mm. pressure; it yields a *nitrate* $C_4H_6N_2,HNO_3$, as colourless crystals melting with decomposition at 110°, and an *aurochloride*, $C_4H_6N_2HAuCl_4$, as yellow prisms melting at 200—201°. When a solution of amidoacetone hydrochloride, obtained by adding isonitrosoacetone to a solution of stannous chloride in strong hydrochloric acid, is successively treated with caustic potash and mercuric chloride, metallic mercury is deposited, and the base is oxidised to *dimethylpyrazine*, $N\!\!<\!\!\begin{matrix}CMe:CH\\ CH:CMe\end{matrix}\!\!>\!\!N$ (compare Abstr., 1892, 507). Amidoaldehyde, when treated with potash and mercuric chloride, is converted in an analogous manner into pyrazine itself (compare this vol., i, 373).

Amidopropyl methyl ketone, $COMe\cdot CHEt\cdot NH_2$, is obtained by reducing isonitrosopropyl methyl ketone with stannous chloride; the *hydrochloride* forms white needles, and melts at 150—151°; the *platinochloride* is a yellow, crystalline powder melting with decomposition at 184°. The base itself is obtained on adding potash to a strong solution of the hydrochloride; it as an oil which quickly solidifies to white crystals. C. F. B.

Pyrimidines Free from Oxygen. By A. PINNER (*Ber.*, **26**, 2122—2125).—*Phenyltetrahydropyrimidine*, $CPh\begin{matrix}N{-}CH_2\\NH{\cdot}CH_2\end{matrix}CH_2$, is prepared by the action of benzamidine on trimethylenic bromide in ether-alcoholic solution at 30—40°. The reaction requires several weeks for completion, and the yield is small, considerable quantities of benzamide and bromopropylbenzamidine being also formed. The pyrimidine decomposes on distillation even under reduced pressure, and, like its simple salts, is a viscid liquid. The *platinochloride*, $C_{10}H_{12}N_2,H_2PtCl_6$, crystallises in yellow prisms melting at 215° with decomposition. Attempts to obtain methylphenylpyrimidine by the action of benzamidine on formylacetone were unsuccessful; benzamidineglycollic acid was the only product which could be isolated.

Acetylacetone readily undergoes condensation with amidines at ordinary temperatures in presence of potassium carbonate; the fatty pyrimidines are viscid liquids, and have not yet been further investigated. The following compounds are prepared by the action of the corresponding amidine on acetylacetone; they are all readily soluble in acids, alcohol, ether, and benzene. *Phenyldimethylpyrimidine*, $CPh\begin{matrix}N{\cdot}CMe\\N{:}CMe\end{matrix}CH$, crystallises in long needles melting at 83°, and boiling at 276°.

Paratolyldimethylpyrimidine, $C_6H_4Me{\cdot}C\begin{matrix}N{\cdot}CMe\\N{:}CMe\end{matrix}CH$, is deposited in silky, lustrous needles; it melts at 128°, and boils at 294°. *Benzyldimethylpyrimidine*, $CH_2Ph{\cdot}C\begin{matrix}N{\cdot}CMe\\N{:}CMe\end{matrix}CH$, forms long needles melting at 80°, and boiling at 274°. *β-Naphthyldimethylpyrimidine*, $C_{10}H_7{\cdot}C\begin{matrix}N{\cdot}CMe\\N{:}CMe\end{matrix}CH$, crystallises in colourless needles; it melts at 116—117°, and boils considerably above 360° without decomposition. *Furyldimethylpyrimidine*, $C_4OH_3{\cdot}C\begin{matrix}N{\cdot}CMe\\N{:}CMe\end{matrix}CH$, is first obtained as an oil which crystallises after some time. It closely resembles the phenyl derivative, melts at 54°, and boils at 263°. J. B. T.

Derivatives of Kyanidine. By J. EPHRAIM (*Ber.*, **26**, 2226—2227).—*Diphenylchlorokyanidine*, $C_3N_3Ph_2Cl$, is obtained by the action of phosphorus oxychloride on diphenylhydroxykyanidine. It forms white needles which melt at 138—139°. The halogen atom of this substance is easily replaced by bases. On treatment with phenylhydrazine at 110°, *diphenylphenylhydrazokyanidine*,

$$C_3N_3Ph_2{\cdot}NH{\cdot}NHPh,$$

is formed; it crystallises in reddish-white needles, and melts at 140°. Aniline produces *diphenylanilidokyanidine*, $C_3N_3Ph_2{\cdot}NHPh$, which forms lustrous, white plates melting at 155°. Alcoholic ammonia acts in a similar manner, producing *diphenylamidokyanidine*, $C_3N_3Ph_2{\cdot}NH_2$, which crystallises in lustrous needles, and melts at 172°.

The halogen atom of diphenylchlorokyanidine, which is combined

with a carbon atom adjacent to a nitrogen atom in a ring containing 3 nitrogen atoms, can therefore be replaced by bases in the same way as the similarly combined halogen atom in rings containing 1 and 2 atoms of nitrogen. A. H.

Constitution of Hypoxanthine and Adenine. By M. Krüger (*Ber.*, **26**, 1914—1922).—From analogy with uric acid and xanthine, one of the following formulæ is deduced for hypoxanthine, $\begin{matrix}NH\cdot CH:C\cdot NH\\ CH:N-C=N\end{matrix}>CO$ or $\begin{matrix}N-CH\cdot C\cdot NH\\ \|\quad\quad|\\ CH\cdot NH\cdot C=N\end{matrix}>CO$, that of adenine being obtained from these by replacing O by NH. Either of these two formulæ also explains the following facts, recently observed by the author. Bromohypoxanthine forms a tetrabromo-additive compound; and, when oxidised with hydrochloric acid and potassium chlorate, yields carbamide and mesoxalylcarbamide. Dimethylhypoxanthine represents the maximum of substitution (of methyl for hydrogen), and, when hydrolysed with dilute sulphuric acid, yields methylamine and methylamidoacetic acid.

Bromohypoxanthine, $C_5H_3BrN_4O$, is obtained by treating bromadenine with nitrous acid. It crystallises with $2H_2O$ as a powder, with $1\frac{1}{2}H_2O$ in tufts of small needles; it may also be prepared by heating dry hypoxanthine with dry bromine at 120°; the immediate product is in this case $C_5H_3N_4OBr,HBr,Br_4$. The *sodium derivative*, $C_5H_2BrN_4ONa + 2H_2O$, forms silky prisms. *Dimethylhypoxanthine*, obtained by heating hypoxanthine with sodium ethoxide, alcohol, water, and methylic iodide, crystallises in silky needles, and with sodium iodide forms a crystalline double salt, $C_7H_8N_4O,NaI + 3H_2O$. C. F. B.

Constitution of Nicotine. By A. Pinner (*Ber.*, **26**, 2135—2137).—A reply to Étard (this vol., i, 675), who considers that the production of an acetyl derivative, which forms a platinochloride, proves the presence of an imide group in nicotine and establishes for it the formula $\begin{matrix}CH:CH\cdot C-CHEt\\ CH:N-C\cdot NH\cdot CH_2\end{matrix}>CH_2$. Working under similar conditions to Étard, the author prepared, several years ago, a substance which appeared to be an additive compound of 1 mol. nicotine and 1 mol. acetic acid, but its homogeneity was open to doubt, and no conclusions can be drawn from its production. Blau has previously pointed out (Abstr., 1891, 583) that if nicotine is represented by Étard's formula, it should yield, on oxidation, hydroxynicotinic acid or amidonicotinic acid, and not nicotinic acid. J. B. T.

Benzoylnicotine. By A. Étard (*Compt. rend.*, **117**, 278—281).—When dry nicotine is mixed with excess of benzoic chloride, there is no action at the ordinary temperature, but if the mixture is heated intermittently to the boiling point of the benzoic chloride, there is an abundant evolution of hydrogen chloride, and benzoylnicotine is formed.

Benzoylnicotine is a colourless and somewhat viscous liquid, which

has no tendency to crystallise. It has a poisonous odour and a feeble taste, very different from that of nicotine, is insoluble in water, and dissolves only in a considerable excess of dilute hydrochloric acid. It is a feeble, monacid base, and the platinochloride is a pale yellow, crystalline compound, of the composition $(C_{10}H_{13}NBz)_2,H_2PtCl_6$.

It follows that, contrary to the general belief, acid chlorides do act on nicotine, and therefore the latter must contain hydrogen in direct union with nitrogen. This view is confirmed by the fact that, when anhydrous nicotine is heated at 160—170° with dry aldehyde, it yields water and a viscous, insoluble base, with all the characteristics of the bases derived from aldehydes, which were discovered by Gerhardt and are commonly known as Schiff's bases.

The author considers that the cotinine and ticonine described by Pinner cannot contain the group NMe, but must contain secondary nitrogen, whilst the apocotinine and the compound $C_9H_{11}NO_4$, obtained from them respectively by reduction, must be regarded as pyridyl-β-butyric derivatives. C. H. B.

Transformation of Quinine. By Z. H. Skraup (*Monatsh.*, **14**, 428—454).—This paper contains a detailed account of the researches formerly noticed in this vol., i, 56, and also the following additional facts. *Normal nichine sulphate*, $(C_{19}H_{24}N_2O_2)_2,H_2SO_4 + 10H_2O$, crystallises in needles; the *acid sulphate*, with $3\frac{1}{2}H_2O$, in colourless prisms; the *acid hydrochloride*, $C_{19}H_{24}N_2O_2,2HCl$, in colourless prisms melting at about 234°; the *acid hydriodide* in yellow prisms melting at 221—222°; the *acid oxalate* in aggregates of minute needles melting at 194°; the *platinochloride* is yellow and amorphous. With hydriodic acid, nichine yields a *trihydriodide*, $C_{19}H_{24}N_2O_2,3HI$, which melts with decomposition at 227°, and is converted by further heating with hydriodic acid into methylic iodide and the compound $C_{18}H_{22}N_2O_2,3HI$, forming yellow needles melting at 219—220°; when heated with alcoholic potash, it is converted into *isonichine*, $C_{19}H_{24}N_2O_3$, which crystallises in white scales resembling benzoic acid, and melts at 208—209°; it yields a *trihydriodide*, and a *platinochloride*,

$$C_{19}H_{24}N_2O_2,H_2PtCl_6,$$

forming orange-red, crystalline aggregates.

With 3 mols. of ethylic iodide, nichine yields a crystalline additive compound, $C_{19}H_{24}N_2O_2,2EtI + 2H_2O$, which melts at 137°; with 1 mol., it yields, not an ethyl compound, but a *basic hydriodide*, $C_{19}H_{24}N_2O_2,HI$, which crystallises in white needles, and melts at 153—154°. With nitrous acid, nichine yields *nitrosonichine nitrate*, $NO{\cdot}C_{19}H_{23}N_2O_2,HNO_3$, crystallising in yellow tables melting with decomposition at 172°, and from which alkalis liberate *nitrosonichine* as a yellowish resin.

Pseudoquinine, $C_{20}H_{24}N_2O_2$, has a specific rotation $[\alpha]_D = -164{\cdot}44°$. The *normal nitrate*, $C_{20}H_{24}N_2O_2,HNO_3 + H_2O$, crystallises in prisms which melt at 130°, and again, after losing water, at 220°; the *basic nitrate*, $(C_{20}H_{24}N_2O_2)_2,HNO_3 + 3H_2O$, in white needles melting at 175—177°; the *normal hydrochloride* $(1\frac{1}{2}H_2O)$, in prisms melting at 256—257°; the *platinochloride*, $C_{20}H_{24}N_2O_2,H_2PtCl_6$, in minute plates. Pseudoquinine

yields, with hydriodic acid, a *trihydriodide*, $C_{20}H_{24}N_2O_2,3HI$, which seems to be identical with that obtained from quinine.

Potassium permanganate oxidises pseudoquinine and nichine with formation of substances analogous to the chitenine obtained from quinine, but whereas quinine yields, in addition, only formic acid, pseudoquinine yields but little formic acid and much acetic acid, and nichine little else but acetic acid. The same thing happens as regards these fatty acids, when chromic acid is used as the oxidising agent; in addition, quinine yields much, pseudoquinine little, and nichine very little, quininic acid. C. F. B.

New Isomerides of the Ethiodides of the Cinchona Alkaloïds. By Z. H. Skraup and F. K. v. Norwall (*Ber.*, **26**, 1968—1970).—By heating the so-called neutral hydriodides of cinchonine, cinchonidine, and quinine with ethylic iodide, crystalline, yellow compounds are obtained of the respective composition

$$C_{19}H_{22}N_2O,HI,EtI \text{ and } C_{20}H_{24}N_2O_2,HI,EtI,$$

which, on being treated with ammonia, yield red, basic compounds, $C_{19}H_{22}N_2O,EtI$ and $C_{20}H_{24}N_2O_2,EtI$; when the latter are heated with a fresh quantity of ethylic iodide, diethiodo-additive compounds are formed more readily than from the alkaloïds themselves.

The new yellow salts are quaternary iodides, and it therefore follows that both the nitrogen atoms in the cinchona alkaloïds are in tertiary combination. As the alkyl iodides of quinoline are yellow, the ethylic iodide of the new derivatives of the cinchona alkaloïds must be in combination with the nitrogen of the quinoline nucleus. A. R. L.

Allocinchonine. By E. Lippmann and F. Fleissner (*Ber.*, **26**, 2005).—The base recently obtained by the authors from hydriodocinchonine dihydriodide (*Monatsh.*, May, 1893), and denominated by them pseudocinchonine, differs from a base described in the meantime by Hesse (this vol., i, 678) under the same name; they therefore propose to call their base *allocinchonine*. It melts at 214—216°, and may be identical with Hesse's apoisocinchonine (*loc. cit.*). However, allocinchonine dihydriodide crystallises with $1H_2O$, whereas the analogous salt of Hesse's apoisocinchonine is anhydrous; the platinochloride of the former is anhydrous, but that of the latter crystallises with $2H_2O$; the sulphates of the two bases also appear to differ. A. R. L.

Dihydroxytropidine. By A. Einhorn and L. Fischer (*Ber.*, **26**, 2008).—*Dihydroxytropidine*, $CH\begin{<}\begin{matrix}NMe\text{———}CH_2\\ CH(OH)\cdot CH(OH)\\ CH_2\text{———}CH_2\end{matrix}\end{>}CH$, is obtained by dropping a solution of potassium permanganate into one of tropidine containing soda and cooled to 0°, driving over the unaltered tropidine from the filtrate with steam, and extracting with ether; it melts at 105°, and the *aurochloride* melts at 235° with decomposition. A. R. L.

Melting Point of Cocaïne Hydrochloride. By O. Hesse (*Annalen*, **276**, 342—344).—Kingel (*Pharm. Zeit.*, **38**, 25) states

that cocaïne hydrochloride melts at 200—202°, and that a lower melting point is indicative of impurities in the sample. The author finds that when the melting point of the pure salt is determined in a Roth's apparatus, or in a sulphuric acid bath, the temperature of which is raised slowly, the value 186° is obtained; whilst when a sulphuric acid bath is used and the temperature is raised rapidly, the salt melts at 200—202°. A. R. L.

Crystalline Form of Scopoline Platinochloride. By A. Ladenburg (*Annalen*, **276**, 345—346).—An answer to Hesse (*Annalen*, **271**, 100). The crystallographic measurements of pseudotropine platinochloride have been already given (Abstr., 1892, 1366). Scopoline platinochloride crystallises in the monosymmetric system, $a : b : c = 0{\cdot}54108 : 1 : 0{\cdot}5489$; $\beta = 119° 45'$. The two bases are therefore distinct compounds. A. R. L.

The Deliquescent Alkaloïd from Lupinus albus. By A. Soldaini (*L'Orosi*, **16**, 109—126).—The author has further examined the deliquescent alkaloïd previously obtained by him from the seeds of *Lupinus albus* (this vol., i, 379). The alkaloid is not decomposed by boiling with 50 per cent. potash, but on heating it with caustic potash at 180°, a heavy, yellow oil with a coniine-like odour distils. This is strongly alkaline, and gives a crystalline, deliquescent *hydrochloride* which melts at 120°, and is soluble in alcohol; the *aurochloride*, $C_{15}H_{22}N_2,HAuCl_4$, forms small, yellow crystals melting at 193—194° with decomposition, and may be crystallised from boiling water without undergoing reduction. The aqueous solution of the residue in the retort gives up a small quantity of an alkaline oil on extraction with ether, and a *platinochloride*, $(C_7H_8N)_2,H_2PtCl_6 + H_2O$, may also be precipitated from it; this substance crystallises in yellow pyramids melting at 240° with decomposition.

On treating the hydrochloride of the original alkaloïd with hydrochloric acid, dehydration occurs, and a deliquescent *hydrochloride* which melts at 154—155° is obtained; the *platinochloride*,

$$C_{15}H_{22}N_2,H_2PtCl_6 + 4\tfrac{1}{2}H_2O,$$

forms reddish pyramids which lose their water at 125—130°, and decompose at 210—212°. The alkaloid seems to contain no methoxyl group, as it does not give methylic chloride when heated in a sealed tube with hydrochloric acid; the action of phosphoric anhydride is similar to that of concentrated hydrochloric acid. No new products were obtained by heating the hydrochloride with soda-lime.

The alkaloïd combines with 4 atoms of bromine in acetic acid solution, giving an unstable compound; this, by spontaneous loss of 1 mol. HBr, yields a substance containing 3 atoms of bromine; the latter, on crystallisation from boiling alcohol, decomposes, yielding the two following compounds. A *hydrobromide*, $C_8H_{13}NO,HBr$, which forms very thin, white crystals melting at 224—225° with decomposition, and a *hydrobromide* melting at 134—135°. The former gives a red, crystalline *aurochloride* which decomposes at 140°, and deposits gold when its pure aqueous solution is boiled. The hydrobromide

melting at 134—135° yields a yellow, crystalline *platinochloride*, $(C_7H_9NO)_2,H_2PtCl_6 + 4\frac{1}{2}H_2O$, which decomposes at 210°; the *hydrochloride* partially melts at 207—210° with decomposition. The *aurochloride*, $(C_7H_9NO)_3HAuCl_4$, is obtained as a yellow powder which softens at 120—122°.

The alkaloïd is reduced by sodium in alcoholic solution, with production of a *hydrochloride* which forms small, soft crystals melting at 158—160° with decomposition. The *aurochloride*, $C_{15}H_{30}N_2O,HAuCl_4$, forms small, yellow crystals which decompose at 145° with evolution of gas.

Phenylhydrazine and hydroxylamine seem to be without action on the alkaloïd; the latter, however, reacts with potassium hydrogen sulphite, giving a product which is still under examination.

W. J. P.

Carpaïne, the Alkaloïd of the Leaves of Carica Papaya, L. By J. J. L. VAN RYN (*Arch. Pharm.*, **231**, 184—211).—The author gives an historical account of the papaw tree, a botanical description of its various parts, and mentions several methods for extracting the alkaloïd from the dried leaves, of which Greshoff's (Abstr., 1891, 334) gives the best results. Carpaïne crystallises in anhydrous, colourless, lustrous prisms melting at 121°, not at 115° as stated by Greshoff, and resolidifies at about 90°; on further heating, it undergoes partial decomposition, some subliming in colourless needles. The alkaloïd is extremely soluble in chloroform and carbon bisulphide, more sparingly in light petroleum and alcohol, and insoluble in water; in alcoholic solution it is dextrorotatory, $[\alpha]_D = +21{\cdot}55°$. The base does not give a colour reaction with sulphuric acid either alone or in presence of bromine water or vanadic anhydride: with potassium chromate and sulphuric acid, a green coloration is produced: nitric acid gives no reaction. The author's analyses of carpaïne agree closely with the formula $C_{14}H_{23}NO_2$; that assigned to it by Merck was $C_{14}H_{27}NO_2$. The *platinochloride*,

$$(C_{14}H_{23}NO_2)_2,H_2PtCl_6,$$

is yellow and crystalline; the *aurochloride* crystallises, with $5H_2O$, in lemon-yellow needles melting at 205°. The hydrochloride darkens at 225°, and decomposes at higher temperatures without melting. The *hydrobromide* is less soluble than the hydrochloride, and crystallises in colourless needles. The *hydriodide* resembles the hydrochloride, and crystallises in groups of pale yellow needles. The *hydrogen sulphate*, $C_{14}H_{23}NO_2,H_2SO_4 + 3H_2O$, is deposited in colourless, prismatic crystals on adding ether to its alcoholic solution. The *nitrate*, $C_{14}H_{23}NO_2,HNO_3 + H_2O$, forms prismatic, crystalline plates.

Ethylcarpaïne, $C_{14}H_{24}NO_2Et$, is prepared by the action of ethylic iodide on the alkaloïd, and treatment of the product with potash; it crystallises from dilute alcohol in colourless, silky, lustrous needles melting at 91°. The compound is not affected by concentrated sulphuric acid or nitric acid, and does not react with Erdmann's reagent or Fröhde's reagent. The *hydriodide*, $C_{14}H_{24}NO_2Et,HI$, crystallises in slender needles melting at 235°, with partial decomposition. The *platinochloride* is a yellow, amorphous salt containing $3H_2O$. The

aurochloride crystallises in lemon-coloured needles melting at 175—176° with partial decomposition. By the action of ethylic iodide on ethylcarpaïne, *ethylcarpaïne ethiodide* is formed; it is crystalline and is not decomposed by soda. The *platinochloride*,

$$(C_{14}H_{24}NO_2Et,EtCl)_2,PtCl_4,$$

crystallises in yellow needles. The *aurochloride* forms lemon-coloured needles melting at 170—171°. It appears from the above results, that carpaïne is a secondary base; an attempt to prepare an ammonium hydroxide from ethylcarpaïne ethiodide was unsuccessful.

Nitrosocarpaïne, $NO\cdot C_{14}H_{24}NO_2$, crystallises from alcohol in colourless prisms melting at 144—145°. The compound is neutral, and exhibits Liebermann's reaction.

Carpaïne does not react with benzoic chloride or acetic chloride, but on treatment with acetic anhydride, a compound is formed which has not yet been investigated. Ammonia and an acid free from nitrogen are formed by the oxidation of carpaïne with sulphuric acid and potassium permanganate. J. B. T.

New Reaction of Eserine, and a Green Colouring Matter derived from it. By S. J. Ferreira da Silva (*Compt. rend.*, **117**, 330—331).—When a minute fragment of eserine or one of its salts is dissolved in a few drops of fuming nitric acid, a yellow solution is obtained, and when this is evaporated on a water bath, it becomes dark yellow, and the residue, when completely dried, is pure green. This reaction is characteristic of eserine, and is very delicate (compare Abstr., 1891, 134). The green substance, which the author calls *chloreserine*, dissolves in water, and also in strong alcohol, forming non-fluorescent, green solutions, from which the original compound can be recovered by evaporation. When dissolved in strong nitric acid, it yields a violet-red solution which afterwards changes to greenish-yellow. The solution in dilute nitric acid is blood-red by reflected light, and greenish-yellow by transmitted light. Ammonia has no effect on the colour of the chloreserine.

When dissolved in water, alcohol, or dilute sulphuric acid, chloreserine shows a well defined absorption band in the red between λ 670 and λ 688, a broader but more nebulous band in the blue and violet between λ 400 and λ 418, and a very feeble band in the orange. C. H. B.

Albumoses and Peptones. By W. Kühne (*Zeit. Biol.*, **29**, 308—324).—The article is mainly polemical, and contests Pekelharing's assertion that peptone is after all only a portion of the albumoses. This view is supported by a number of fresh experiments, in which the different behaviour of peptones and albumoses towards metaphosphoric and trichloracetic acids is the main point. W. D. H.

Proteïds of Wheat. By T. B. Osborne and G. Voorhees (*Amer. Chem. J.*, **15**, 392—471).—This paper contains an historical review of the subject, and a detailed account of the compounds extracted from various grades of wheat flour by dilute alcohol, water, a 10 per cent.

sodium chloride solution, and dilute potash, together with the methods adopted for precipitation, isolation, and estimation. The following is an abstract of the summary which is appended.

Wheat contains the following proteïds. (1.) A globulin belonging to the class of vegetable vitellins, soluble in saline solutions, precipitated by dilution and by saturation with magnesium sulphate or ammonium sulphate, but not with sodium chloride, not coagulated below 100°, and only partially at that temperature. This proteïd amounts to 0·6—0·7 per cent. of the wheat, and when dried at 100°, has the following percentage composition:—C 51·03, H 6·85, N 18·39, S 0·69, O 23·04. (2.) An albumin, coagulating at 52°, in which condition it contains, per cent., C 53·02, H 6·84, N 16·80, S 1·28, O 22·06. It differs from animal albumin in that its solutions are precipitated by saturation with sodium chloride or magnesium sulphate; it is not precipitated by dialysis. From 0·3 to 0·4 per cent. of it is present in wheat. (3.) A proteose, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturation with sodium chloride. On concentrating its solutions by ebullition, a coagulum was gradually developed; this constituted about 0·3 per cent. of the wheat, and contained, per cent., C 51·86, H 6·82, N 17·32, S and O 24·00. The filtrate from this proteose contained a similar substance to the extent of 0·2—0·4 per cent. of the seed, but it was not obtained in a pure condition. (4.) Gliadin, soluble in dilute alcohol, and forming about 4·25 per cent. of the seed. It contains, per cent., C 52·72, H 6·86, N 17·66, S 1·14, O 21·62. This compound is the gliadin of Taddei, and the plant gelatin of Dumas and Cahours. In an impure state it has been described by others as gluten, fibrin, gliadin, mucedin, insoluble phytalbumose, and mucin. It dissolves in distilled water to an opalescent solution, from which it is precipitated by the addition of sodium chloride. It is insoluble in absolute alcohol, but very soluble in 70—80 per cent. alcohol; water or strong alcohol precipitates it from this solution. It dissolves in very dilute acids and alkalis, and is precipitated from these solutions unchanged by neutralisation. This proteïd is one on which the formation of gluten largely depends. (5.) Glutenin, insoluble in water, saline solutions, and dilute alcohol. This constitutes the remainder of the proteïds of wheat, and amounts to 4—4·5 per cent. of the seed. It is soluble in dilute acids and alkalis, and is precipitated from such solutions by neutralisation. For purification, it is dissolved in 0·2 per cent. potash, precipitated by neutralisation, extracted with alcohol and ether, again dissolved in potash, the solution filtered, and once more precipitated. When thus prepared and dried at 110°, it contains, per cent., C 52·34, H 6·83, N 17·49, S 1·08, O 22·26. The same proteïd has been named by others zymone, plant fibrin, gluten-fibrin and gluten-caseïn. (6.) Wheat gluten is composed of gliadin and glutenin as essential constituents. The gliadin with water forms a sticky medium, which is not wholly soluble in the presence of salts; the flour is bound by this medium, and the dough and gluten are rendered tough and coherent by it. The glutenin imparts solidity to the gluten, forming a nucleus to which the gliadin adheres, and from which it is not washed away by water.

Gliadin and starch, mixed in the proportion of 1 : 10, form a dough, but no gluten, so that the gliadin is washed away with the starch. Flour free from gliadin gives no gluten. Soluble salts are also essential to the formation of gluten, as gliadin is readily soluble in distilled water; the mineral constituents of the seed are sufficient to supply the necessary salts. (7.) No fermentative action occurs in the formation of gluten, for its constituents are found in the flour having the same properties and composition as in the gluten, even under those conditions which would be supposed completely to remove antecedent proteïds, or to prevent fermentative action. All the phenomena heretofore attributed to ferment action are explained by the properties of the proteïds themselves as they exist in the seed and in the gluten.

A. G. B.

Solutions of Fibrin. By M. Arthus and A. Huber (*Arch. physiol.*, 1893, 447—454).—It is stated that saline solutions of fresh fibrin, especially in 1 per cent. solution of sodium fluoride, exhibit properties similar to those obtained when fibrin is digested by gastric or pancreatic juice. Fibrin coagulated by heat, or by alcohol, is not soluble in solutions of neutral salts. W. D. H.

Composition of Hæmatin and of Hæmatoporphyrin. By M. Nencki (*Chem. Centr.*, 1893, ii, 95—96; from *Arch. sci. biol.*, **2**, 121—131).—A reply to various criticisms of the author's previous work on the subject. Hoppe-Seyler's crystalline hæmatin contains acetic acid (compare *Ber.*, **18**, 601), that of the author amyl alcohol; the difference is due merely to the method of preparation.

J. B. T.

Wheat Diastase. By I. V. Egoroff (*J. Russ. Chem. Soc.*, **25**, 80—83).—Diastase was prepared by moistening wheat at 8°, and allowing it to germinate in the dark at 16°, the air-dried malt being then ground up and treated for 24 hours with twice its weight of alcohol of 30°. From the alcoholic extract, the diastase was precipitated in three portions by means of absolute alcohol, each portion being washed and dried separately. Fractionation was then pursued by dissolving in water and precipitating with alcohol, until the starch and albumen had been almost entirely removed. From 3500 grams of wheat, only 4 grams of diastase were obtained. Analysis yielded the following results.

		Calculated for ashless material.
Hydrogen	6·78 per cent.	7·1 per cent.
Carbon.....	40·24 „	42·18 „
Nitrogen	4·7 „	4·93 „
Sulphur.....	0·7 „	0·74 „
Phosphorus	1·45 „	—
Ash.....	4·6 „	—

Wheat diastase thus prepared is a white powder, with a faint, yellowish tint, and dissolves in water with formation of a slightly

opalescent solution. With guaiacum and peroxide of hydrogen, it gives a dark-blue coloration. Neither 75° alcohol, nor half-saturated salt solution, will extract diastase from gluten. J. W.

Reychler's "Artificial Diastase." By I. V. EGOROFF (*J. Russ. Chem. Soc.*, **25**, 83—86).—The author has made experiments which show that by dissolving gluten in 0·2 per cent. potassium dihydrogen phosphate, or in 0·1 per cent. acetic acid, no fresh diastase is formed, and that the greater power possessed by these over aqueous solutions of converting starch into maltose is probably due to the development of a bacterium capable of effecting this fermentation. J. W.

Diastase. By N. LUBAVIN (*J. Russ. Chem. Soc.*, **25**, 86—90).—The author confirms the observations made in the foregoing paper. J. W.

A Ferment in Penicillium glaucum resembling Emulsin. By E. GÉRARD (*J. Pharm.*, [5], **28**, 11—12).—The impure mixture of ferments isolated by the usual process from mature *Penicillium glaucum* inverts cane sugar and converts starch into sugars, and, in addition, completely hydrolyses the glucosides, amygdalin and salicin. From the latter property, the presence of a ferment resembling emulsin is inferred. W. T.

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